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PB-266 241

Extraction of Chemical Pollutants from Industrial Wastewaters with Volatile Solvents

California Univ, Berkeley Dept of Chemical Engineering

Prepared for

Robert S Kerr Environmental Research Lab, Ada, Okla

Dec 76

PB 266 241

EPA-600/2-76-220
December 1976

Environmental Protection Technology Series

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NATIONAL TECHNICAL
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U. S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

TECHNICAL REPORT DATA

(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA-600/2-76-220	2.	3. RECIPIENT'S ACCESSION NO.
4. TITLE AND SUBTITLE Extraction of Chemical Pollutants from Industrial Wastewaters with Volatile Solvents		5. REPORT DATE December 1976 (Issuing Date) 6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) Jonathan P. Earhart, Kwang W. Won, C. Judson King, and John M. Prausnitz		8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Department of Chemical Engineering University of California Berkeley, CA 94720		10. PROGRAM ELEMENT NO. 1BB610 11. CONTRACT/GRANT NO. R801030
12. SPONSORING AGENCY NAME AND ADDRESS Robert S. Kerr Environmental Research Lab. - Ada, OK Office of Research and Development U.S. Environmental Protection Agency Ada, Oklahoma 74820		13. TYPE OF REPORT AND PERIOD COVERED Final 1971-1975 14. SPONSORING AGENCY CODE EPA/600/15

15. SUPPLEMENTARY NOTES

16. ABSTRACT

Solvent extraction with volatile solvents was studied as a method for treating wastewaters from petroleum refineries and petrochemical plants. Extraction is most attractive when the loading of organics is high, when substances are present which pose difficulties for biological oxidation, and/or when the chemical value of recovered organics is high. Volatile solvents (isobutylene and isobutane) were given particular attention, since they are easily regenerated and since they have a low solubility in the effluent water. Equilibrium distribution coefficients were determined for numerous systems of water, various solvents and various solutes, and correlations of these coefficients were developed. A miniplant extraction facility was used to demonstrate the capabilities of extraction for treatment of seven different industrial wastewaters, and for the purpose of analyzing the underlying mass transfer and axial mixing behavior. The scale-up of the extraction system and the logic of selecting extraction processes for wastewater treatment are explored at length.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
*Water Pollution *Solvent Extraction Solvents Extractors Wastewater	Selected wastewaters from refining & petrochemical processes. Volatile solvent extraction Dual solvent extraction Rotating disc contactor Design considerations for scale-up.	07A

18. DISTRIBUTION STATEMENT Release to Public	19. SECURITY CLASS *(This Report)* unclassified	21. NO. OF PAGES 531
	20. SECURITY CLASS *(This page)* unclassified	22. PRICE PC-A23/MF-A01

EPA Form 2220-1 (9-73)

U.S. GOVERNMENT PRINTING OFFICE: 1977— 757-056/5545

EPA-600/2-76-220
December 1976

EXTRACTION OF CHEMICAL POLLUTANTS FROM INDUSTRIAL WASTEWATERS WITH VOLATILE SOLVENTS

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ADA, OKLAHOMA 74820

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FOREWORD

Man and his environment must be protected from the adverse effects of toxic and hazardous chemicals, metals, and other forms of pollution; including the unwise management of residuals. Efforts to protect the environment require a focus that recognizes the interplay between the components of our physical environment--air, water, and land. The Robert S. Kerr Environmental Research Laboratory contributes to this focus through multidisciplinary programs engaged in

- studies on the removal of environmental contaminants from waste discharges to the environment, and
- the search for ways to prevent contamination and to recycle valuable resources.

The information presented in this grant report is the culmination of research on a method designed to reduce the contaminent load of certain industrial wastewaters and recover valuable chemicals.

ABSTRACT

This report presents the results of an experimental study and general process evaluation of the extraction of organic pollutants from wastewaters from petroleum refineries and petrochemical plants, using volatile solvents. Three basic approaches are considered; the first uses a single extraction step with a volatile solvent; the second uses successive extractions with a less volatile, polar solvent followed by extraction with a volatile solvent; and the third uses extraction with a mixture of polar solvent and volatile solvent, followed by extraction with the volatile solvent alone. The principal volatile solvents considered are isobutylene and isobutane.

Equilibrium distribution coefficients were measured for numerous solutes distributing between water and various solvents. These reflect solvent capacities and selectivities.

A miniplant extraction system was constructed, using both RDC and spray-column extractors, coupled with solvent circulation and regeneration systems. The miniplant was used to test and demonstrate extraction processes for seven different real industrial wastewaters, and for various synthetic waters.

Volatile-solvent extraction is evaluated and compared with other competitive means of handling high-oxygen-demand wastewaters -- e.g., steam stripping -- and is found to be economically promising for cases where the organics

load is high, where recovery of organic solutes is desireable, or where the water presents special problems for biological treatment systems.

This report was submitted in fulfillment of Grant No. R801030 by the University of California, Department of Chemical Engineering, under the sponsorship of the Environmental Protection Agency. Work was completed as of September 1975.

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ACKNOWLEDGEMENTS

This work was carried out in the Department of Chemical Engineering of the University of California, Berkeley, California. In addition to the principal authors, important contributions were made by Richard K. Herz, Ho-Yan Wong and James M. Wardell, all acting as Research Assistants, and by James N. Michaels and Stephen Loftus, acting as Laboratory Helpers. Thanks are also due to the support staff of the College of Chemistry, notibly the shops, for their contributions of services and advice, and to Ms. Bonni Maunder for her conscientious typing of this report. We are also grateful for the frequent advice and assistance of Messrs. L. Frank Mayhue and Jack H. Hale of the EPA staff.

SECTION I

CONCLUSIONS

Solvent extraction is attractive for treatment of wastewaters from petroleum refining and petrochemical plants in cases where there is a high value of recovered chemicals, where constituents of the water pose special problems for biological treatment, and/or when a particular water stream has a much higher organics content than other wastewaters from the plant. A principal advantage of solvent extraction is the opportunity for recovery, rather than degradation, of dissolved and suspended organics.

Volatile solvents are attractive for extraction processes for wastewater treatment because of their low solubility in water at atmospheric pressure and because of their ease of regeneration. An analysis of candidate volatile solvents points toward the general attractiveness of C_4 hydrocarbons -- e.g., isobutylene and isobutane.

Measurements of equilibrium distribution coefficients and miniplant extraction runs show that direct extraction with volatile solvents is effective in many cases. There is a strong economic incentive for the use of relatively low ratios of solvent flow to water flow, e.g., 0.1. Because of this, there is often an incentive for dual solvent processes, wherein a less volatile, polar solvent is used to remove the primary pollutants from water and then a volatile solvent is used to remove residual amounts of the polar solvent. This may be accomplished by contacting the water with the two solvents sequentially, or by contacting the water first with a mixture of the solvents, followed by extraction with the volatile solvent alone.

The miniplant was used to carry out solvent-extraction treatment of seven real, industrial wastewaters. (1) High removals of phenol, cresols and COD were obtained from a lube-oil refining wastewater by dual-solvent extraction using n-butyl acetate and isobutylene. (2) A substantial reduction in COD was obtained for a condenstate from a process manufacturing cresylic-acids from spent caustic, using direct extraction with isobutylene. (3) For quench water from an ethylene plant, a considerable reduction in COD and effective removal of suspended solids were obtained using direct extraction with isobutane. (4) For wastewater from an oxychlorination ethylene-dichloride plant, chloral was effectively removed using octanol as a solvent; the effluent is then subjected to isobutane extraction for octanol removal. It was found that extraction with octanol is rate-limited by a chemical reaction of chloral with the solvent. (5) For wastewater from the manufacture of phenol-formaldehyde resins, effective removal of phenol was achieved by dual-solvent extraction using n-butyl acetate and isobutylene. (6) Dissolved organics were effectively removed from a hydrofiner condensate water by extraction with methyl isobutyl ketone, followed by volatile-solvent extraction for reclamation of the ketone solvent. (7) For wastewater from styrene manufacture, very complete removal of dissolved aromatics and COD was achieved by extraction with isobutylene. Scale-up procedures for industrial units were considered. These reflect key variables for further study and show the desirability of on-stream pilot testing with much higher water throughputs than could be used in the present work.

In some cases, suspended solid material was effectively removed during extraction with isobutylene or isobutane; in other cases it was not. Factors leading to effective removal of suspended solids in wastewater extraction processes deserve further study.

SECTION II

RECOMMENDATIONS

1. The results obtained in this work are highly encouraging. It is now evident that double-solvent extraction (one polar solvent, one volatile nonpolar solvent) and, in some cases, direct volatile-solvent extraction provide a promising and economic technique for removal of organic pollutants from industrial wastewaters. Therefore, this technique merits further study toward development of a large-scale process suitable for industrial application.

2. One area in which we do not have a good understanding of the fundamentals involved is in the removal of dispersed liquid pollutants. With the ethylene quench waste water, the dispersed organics were not removed by isobutylene extraction but were well removed by isobutane extraction. A study of the factors which make for good coalescence between solvent and pollutant droplets would help determine when dispersed pollutants could be recovered by solvent extraction.

3. Several families of organic solutes are similar to phenol and acetic acid with respect to the difficulties in recovery by steam stripping. Further work is needed to

determine which polar solvents would be good for these solutes in a dual solvent process. The organic acids from propionic to pentanoic would be solutes which are particularly promising candidates for recovery by dual solvent extraction.

4. Finally, the need for an intermediate-scale pilot plant study is discussed in Section IX. In addition to providing data for scale-up to a commercial RDC extractor, such a study would be useful in determining the validity of the general correlations describing the operation of an RDC. In particular the unexpectedly low removal found in this work for solutes having an extraction factor less than 1 should be investigated further. By using an RDC extractor with sample points all along the column, the validity of the axial dispersion model for cases where E is less than 1 could be checked. Answers to these uncertainties would improve our ability to evaluate the cost of an RDC extractor in the treatment of many additional waste water streams.

SECTION III

INTRODUCTION AND BACKGROUND

This report deals with solvent extraction as a method of removal of pollutants from waste waters from petroleum refining and petrochemical manufacture processes. Attention is confined, for the most part, to removal of organic solutes. The use of volatile solvents is emphasized, either alone or in combination with other solvents.

Categories of Waste Water Treatment Processes.

Even when we limit consideration to organic pollutants in industrial waste waters, there are a variety of possible processing techniques. These processes can be categorized into two broad groups. First, there are the non-recovery techniques. In these processes no attempt is made to recover the pollutants in a concentrated form to help offset the processing costs associated with waste treatment. Some examples of non-recovery processes are biological oxidation, carbon adsorption with thermal-oxidative regeneration, direct incineration, deep well injection, and solvent extraction where the loaded solvent is either destroyed (e.g., by burning) or recycled to some part of the plant where the pollutants are destroyed by existing process steps.

The second category of waste water treatment processes is the recovery techniques. In these processes the pollutants are recovered in a concentrated form so that they may be sold or used to replace the purchase of make-up chemicals. Some examples of recovery processes are solvent extraction with a secondary separation process to regenerate the solvent, steam stripping, and carbon adsorption with caustic washing for regeneration. The processing costs are generally higher than for the non-recovery processes because of such factors as the cost of distilling a loaded solvent stream, the cost of heat to raise the entire water stream to its boiling point, or the cost of required chemicals. Thus the recovered pollutant must be of sufficient value and quantity for a recovery technique to be economically competitive with a non-recovery process.

Although there are many possible waste water processing techniques, the petroleum, petrochemical and organic chemical industries presently rely extensively on biological oxidation processes (Beychok, 1967). Those aqueous process effluents which have an appreciable biological oxygen demand are usually combined and treated in a central facility. Only the most highly contaminated, toxic, or non-biodegradable streams are treated on an individual basis. The potential advantage of pollutant recovery from many of these individual streams has recently been described (Fox, 1973).

General Considerations in Solvent Extraction for Waste Water Treatment.

The application of solvent extraction to selected water effluents from individual processes can produce valuable recovered pollutants, can solve problems with non-biodegradable or toxic pollutants, and will reduce the load on the central biological oxidation plant. However, the cost of waste treatment will make solvent extraction feasible only when applied to certain water effluents.

The cost to process a given flow of polluted water by biological oxidation or carbon adsorption tends to increase as the pollutant concentration increases. This increase in cost results from the need to supply more oxygen and to provide a greater residence time for biological oxidation, or from the need to regenerate the carbon more frequently. However, the cost to remove a fixed fraction of the pollutants from a given flow of polluted water by solvent extraction tends to remain approximately constant as the pollutant concentration increases since the necessary solvent flow does not change greatly. Also, the profit from recovered pollutant increases proportionally to the concentration of pollutant. These factors tend to make solvent extraction most economical when applied to the most highly contaminated streams and biological oxidation or carbon adsorption best for dilute streams. One of the goals of this work is to identify particular pollutants and particular waste water problems which will be most economically controlled by solvent extraction.

Solvent extraction has been infrequently applied to waste water treatment. The principal application has been for the recovery of phenol and higher molecular weight phenolic compounds. Other applications include acetic acid recovery and oily water treatment. The reasons for this limited application include: (1) the losses of solvent due to its solubility in the purified water can result in unacceptable costs for solvent make-up or solvent recovery, (2) the equipment and energy for solvent regeneration can be very expensive, and (3) synthesizing a good process requires the designer to choose from a large number of alternatives such as type of solvent, type of extractor, method of solvent regeneration, and method of solvent removal from the purified water. One approach to minimizing solubility and regeneration costs is to use a very volatile, slightly soluble solvent like isobutane. Development of this approach has been a major part of this research.

Another factor which may have constrained the development of solvent extraction processes is the need to identify the chemical nature of the major pollutants present in the waste water to be able to evaluate and understand this advanced processing technique. There is a considerable literature describing waste streams from petroleum (Beychok, 1967) and chemical (Jones, 1971) industries, but the waste waters are usually characterized in terms of overall pollution impact parameters such as biological oxygen demand (BOD), chemical oxygen demand (COD), turbidity, dissolved solids, and oil concentration. The phenol concentration is the only individual pollutant often identified, and this usually includes all phenolic compounds instead of only phenol. In the combined streams feeding the central biological oxidation process, the identification of individual pollutants is difficult because of the large number of pollutants present. However, for an individual stream where the number of major pollutants is much smaller, techniques such as those based on gas chromatography either with flame ionization detection (Herz, 1972) or in conjunction with mass spectroscopy or infrared analysis (Sugar and Conway, 1968) have been successfully used. Also, the company that developed the offending process should be able to provide a list of the pollutants most likely to be present. With these approaches now available, pollutant identification should not be a limiting constraint to process development.

Previous Applications of Solvent Extraction for the Recovery of Phenolic Compounds.

The extensive literature on the removal and recovery of phenolic compounds by solvent extraction has recently been reviewed (Kiezyk and MacKay, 1971). By considering the details of the various processes which have been developed for recovery of phenol and other pollutants, we can begin to develop generalizations about the application of solvent extraction. Phenol is a particularly severe organic pollutant not only because of its contribution to the BOD of the waste water, but also because it imparts a medicinal taste and odor to drinking water which can be detected in the concentration range 0.05

to 0.10 ppm and, when the water is chlorinated, the resulting chlorinated phenols can be detected at about 0.005 ppm (Beychok, 1967).

First consider the physical characteristics of phenol which have led to its preferred treatment by solvent extraction. In biological oxidation processes, special precautions must be taken since the oxidation bacteria may be killed by phenolic concentrations over 50 ppm (McKinney, 1967). However, in the waste waters from the by-product coke industry, from phenolic resin manufacture, from phenol production plants, and from certain petroleum refining operations, the concentration of phenolic compounds can be several thousand ppm or higher. At these concentrations a recovery process should be favored. Phenol forms a minimum boiling azeotrope with water which contains only 9.2 weight % phenol (Weast, 1970), so steam stripping will not be as successful as it is in other applications. Carbon adsorption with chemical regeneration has been applied (Fox, 1973), but the processing costs become large at such high concentrations. Solvent extraction of phenol may be the best process primarily because all other alternatives are more expensive for phenol removal than with other, more common pollution problems.

The earliest large-scale use of solvent extraction for phenol recovery was associated with the by-product coke industry in Germany. Rhodes (1949) gives a detailed description of the three types of solvent extraction processes which were developed. The earliest process used benzene to extract phenolics from the waste water from coke ovens. Initially the phenol was recovered by distillation, but this proved too costly and later regeneration of the benzene utilized a back-extraction into a sodium hydroxide solution. The process thus recovered the phenolics as a concentrated aqueous solution of sodium phenolate. Eighteen of these plants were still in use in 1968 (Wurm, 1968). The second process used tricresyl phosphate as a solvent for phenol extraction. This solvent has a distribution coefficient for phenol about 8 times larger than that for benzene (Tupholme, 1933); therefore, a smaller volume of solvent per unit of water treated was possible. Distillation was used to separate the phenolics from the solvent. Since tricresyl phosphate has a very high boiling point, vacuum distillation was used, and the phenol was recovered as the distillate. This resulted in a very pure phenol product, but less volatile phenolics and other organics tended to build up in the recirculated solvent causing problems of increased viscosity and decreased phenol capacity. These problems led to the failure of this process after it was applied for a short time in several small plants in Germany.

The third process described by Rhodes is known as the Phenolsolvan process. This process is still being offered commercially, and it will likely be used in several of the presently planned coal gasification projects which utilize Lurgi gasifiers (Beychok, 1974). The solvent initially used was isobutyl acetate which has a capacity for phenol extraction about 3 times better than that of tricresyl phosphate. In the late 1950's a number of process changes were incorporated including a change in solvent to isopropyl ether. Although this change resulted in a 60% reduction in distribution coefficient, the advantages of lower cost and of higher volatility both in solvent regeneration and in solvent recovery from the purified water were claimed to justify the change (Wurm, 1968).

The solubility of isopropyl ether is about 8000 ppm; therefore, it must be recovered from the purified water. As shown in Figure 1 (Wurm, 1968), this need for solvent recovery complicates the process. The primary step is the countercurrent contacting of feed water with regenerated isopropyl ether in a multiple-stage mixer-settler. The loaded solvent is then regenerated in a two-stage distillation column, D, where the lower portion operates as a steam stripper to remove traces of solvent from the product phenolic mixture. The three absorbers, A, B, and C, are used for recovering dissolved solvent. In C the isopropyl ether is stripped from the purified water using an inert gas. The isopropyl ether is next absorbed from the inert gas by contacting with phenol in B. The small amount of phenol picked up by the inert gas is then absorbed into the feed water in A. Several other methods of dissolved solvent recovery including steam stripping and extraction with xylene have also been developed, but the illustrated process is the preferred arrangement for treating coke oven condensate (Wurm, 1968).

During petroleum refining, phenolic waste waters are generated from catalytic and thermal cracking operations. This water, which typically

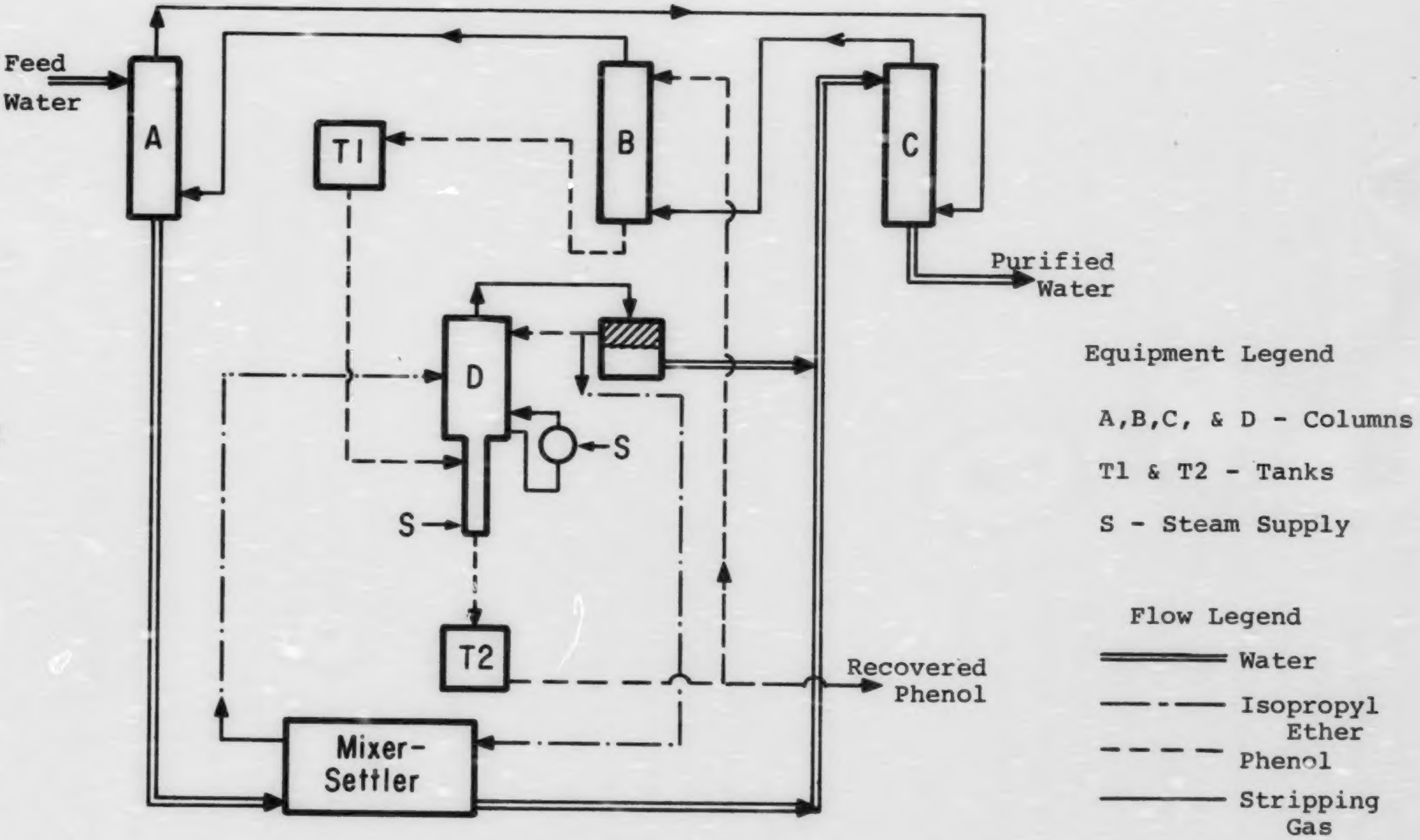


Figure 1. The Phenosolvan Process

contains about 300 ppm of phenolic compounds, has been extracted either with crude oil or with light catalytic cycle oil to remove most of the phenolics. The operation using crude oil is actually a modification of the normal crude oil desalting operation where a waste water rather than fresh water is used to remove salt from the incoming crude oil (Beychok, 1967). The extracted phenols are subsequently destroyed in downstream refinery operations. The process using light catalytic cycle oil is offered to the petroleum industry under the Phenex trademark (Lewis, 1968). The cycle oil after treatment is blended with distillate fuels where the phenols are beneficial in inhibiting oxidation and improving color stability. In both cases, the extraction is conducted in a mixing valve followed by an electrostatic coalescer. Since the phenols are not recovered in either process, these techniques are examples of solvent extraction in a non-recovery process.

About half the U. S. production of phenol is by the cumene process in which cumene is reacted with air to produce phenol and by-product acetone (Stobaugh, 1966). Several side-products including mesityl oxide are also produced, and a waste water stream containing phenol and acetone is generated. A logical route for reducing the pollutant content of this waste water is extraction using the reactant cumene stream as the solvent (Witt and Forbes, 1971). Bewley (1969) has determined that a mixture of 20% mesityl oxide in cumene will increase the phenol distribution coefficient about 10 times over that for pure cumene. The loaded cumene will contain phenol, mesityl oxide, and acetone, all of which are normal products of the cumene-to-phenol reaction. Therefore, the existing separation sequence used in the main process can equally well serve to regenerate the phenol extraction solvent at a minimal increase in cost. Since the recovered phenol ends up in the primary product, this is a recovery technique with a unique opportunity for solvent regeneration in the main processing equipment.

Recovery of Non-Phenolic Pollutants by Solvent Extraction.

The recovery of acetic acid from the effluent water from cellulose acetate manufacture and from semi-chemical pulping plants is of significant economic importance (Brown, 1963). These waste waters contain sodium acetate at 2-20%. After acidification, the resulting acetic acid can be economically recovered by solvent extraction. The black liquor from semi-chemical pulping plants is extracted with methyl ethyl ketone for the recovery of both acetic and formic acids (Weaver and Biggs, 1961). The cellulose acetate waste water is usually extracted with ethyl acetate, although ethyl and isopropyl ether have also been used. In this application, the simultaneous extraction of water is a very important consideration, and the steps in solvent regeneration and acetic acid concentration often involve azeotropic distillations. Acetic acid extraction is more difficult than phenol extraction in that the distribution coefficients are much lower.

Two processes have been developed which use solvent extraction for the treatment of oily waste waters. Strausser and Kurland (1970) have patented a process for the purification of ethylene plant process quench water. This quench water contains a very stable emulsion of aromatic hydrocarbons, light olefinic polymers, suspended heavy tar polymers, and coke particles. The water stream is contacted in a mixer-settler with an aromatic distillate which contains 40 to 70% benzene and which is a natural by-product of the ethylene production process. The extraction after complete settling and filtration produces a water suitable for recycle to the quench tower. The loaded aromatic solvent is separated from the extracted tars in the existing distillation train. King (1970) has patented a similar process for treating the aqueous condensate from styrene manufacture. The condensate from the dehydrogenation of ethylbenzene to produce styrene contains a small quantity of dissolved styrene which tends to polymerize and plug the process equipment. In this extraction process, the water is treated with fresh ethylbenzene which extracts the styrene into the organic phase where it is less likely to polymerize. The loaded solvent is recycled to the dehydrogenation reactor, and the water is steam stripped to recover dissolved ethylbenzene. Both processes recover the pollutants by using an existing process stream as solvent and existing distillation equipment for regeneration.

Two other applications of solvent extraction for waste water treatment are mentioned by Jones

(1971) without details. The aqueous effluent from a rubber processing plant was treated by extraction with benzene for the removal of thiazole. Salicyclic acid and other hydroxy aromatic acids were extracted from a waste water using methyl isobutyl ketone.

The preceding discussion comprises the known applications of solvent extraction for industrial waste water treatment. Clearly there must be many other organic chemicals that cause problems by their presence in an aqueous effluent but that are not now treated by solvent extraction. One of the objectives of this research is to determine if there are fundamental barriers which have limited wider application of solvent extraction.

Types of Extraction Devices.

The number and variety of liquid-liquid contactors that have been proposed is considerable, varying from the simplest spray towers to high-performance centrifugal types. The well-established extractors are described in the standard works (Treybal, 1963) and in several review articles (Hanson, 1968; Akell, 1966; Reman, 1966). The special requirements for use in treating waste water do not eliminate many types of extractors from consideration, although the presence of solid particles in a waste water stream might cause plugging problems in a packed tower.

For the recovery of phenol, commercial installations using a packed column extractor (Edmonds and Jenkins, 1954), a pump-mix mixer-settler (Wurm, 1968), and a rotating disc contactor (Misek and Rozkos, 1966) have been described. The use of a centrifugal extractor for phenol recovery has also been recommended (Kaiser, 1955). In the Phenex process (Lewis, 1968) a mixing valve followed by an electrostatic coalescer is used. A packed column of special design to overcome fouling problems has been used in the recovery of acetic acid from pulping waste water (Weaver and Biggs, 1961). Mixer-settlers are the suggested type of extractor for oily water treatment (Strausser and Kurland, 1970).

Objectives of This Research.

The goals of this project were (1) to generate sufficient data so that a realistic economic evaluation can be made for the use of solvent extraction on selected actual waste waters, (2) to determine in what cases the use of a volatile solvent like isobutane can lead to better economics, (3) to identify types of extractors that are likely to be most useful, and (4) to try to generalize the procedures for choosing a "good" solvent extraction process. We expect this study to help identify cases where solvent extraction should be a promising alternative to the present treatment method. The approach has been a combination of conceptual process designs, experimental extractions of actual and synthetic waste waters, and measurement and correlation of equilibrium distribution data.

Since the present state-of-the-art of solvent extraction almost always requires pilot-scale study when developing a new process (Treybal, 1966), a small pilot plant was built and used to study many different organic pollutants and several different solvents. Realizing that the use of actual waste water may uncover problems in process development which were not apparent when treating synthetic mixtures of solutes in water, we contacted several companies and asked for information on their particular waste water problems. Generally these contacts were productive and in some cases resulted in our being provided with large samples of actual waste water which could be treated in the pilot plant. The results of these and other experiments are described in succeeding sections.

SECTION IV
GENERAL PROCESS CONSIDERATIONS

The net cost of waste treatment is the primary basis for choosing between feasible alternative processes. If any recovery process is to be preferred over biological oxidation for the elimination of a biodegradable pollutant, then the value and quantity of the recovered pollutant must be substantial. Because of the large volume of water to be treated, a relatively low concentration of only 1% pollutant in water can lead to a significant value. This can be simply illustrated for the case of phenol when it is assumed that 95% of the feed phenol is recovered and sold at one-half the current market price of 9-1/2 cents/lb. The value of the recovered pollutant is $3.75 per thousand gallons of water, quite a substantial value.

The above estimate is conservative as compared to the general case because many pollutants are more valuable than phenol. Sale at one-half market price, which was assumed since the pollutant will likely be impure, is also conservative for cases where the recovered pollutant is simply added back to the main process. For example, this direct recycle would be feasible if the recovered pollutant is a product of the main process or is a solvent in the main process. From these approximate considerations we would expect that a general purpose recovery process which could be operated for several dollars per thousand gallons of water treated would be a useful alternative to biological oxidation. Steam stripping and solvent extraction are two such processes.

Considerations Pertaining to Steam Stripping

Steam stripping is a general purpose waste treatment process because at low concentrations most dissolved organic chemicals are more volatile than water. However, to avoid a vacuum column, the entire waste water stream must be heated to the atmospheric boiling point. This requires a substantial amount of energy (e.g., as steam), although some of this heat can be recovered in a feed-bottoms heat exchanger. If the waste water stream is corrosive, increasing the temperature as required in steam stripping will aggravate the problem.

Generally with all but the lowest molecular weight organic compounds, an azeotrope will occur at some concentration in the water-pollutant binary system. Although the process is referred to as steam stripping, reflux will be required to produce a recovered organic stream with a concentration approaching the azeotropic composition. The process is actually a distillation, and the azeotrope limits the purity of the concentrated organic product. With the higher molecular weight compounds, the critical solution temperature will be above the binary atmospheric azeotropic temperature, and a heterogeneous azeotrope will be formed. This generally makes the separation easier because, when the distillate condenses, two phases are formed. The organic phase can be taken as the recovered pollutant product, and the water phase can be either mixed with the feed or used as reflux.

The above description refers to dissolved organic pollutants in water. When the organic pollutant is present as a liquid dispersion, then its removal by steam stripping may be more difficult. Unless the organic phase separates from the water in the distillate, the greatest purity of recovered pollutant is determined by the relative vapor pressures of water and pollutant. When a vapor mixture of a highly insoluble organic and water is condensed, the resulting liquid may be an emulsion of very fine organic droplets suspended in the water. When this is the case, the waste water problem is not yet solved.

A process which recovers dissolved n-butyl acetate from a large flow of water is shown in Figure 2. This binary system forms a heterogeneous azeotrope, and advantage is taken of this fact in the process arrangement. One source of such a waste water is a process which uses n-butyl acetate as solvent for the extraction of phenol. Another source of this type of waste stream but at a much smaller flow rate is an n-butyl acetate production plant which is based on the following reaction:

$$n\text{-}C_4H_9OH + CH_3COOH \longrightarrow n\text{-}C_4H_9OOCCH_3 + H_2O.$$

The waste stream contains water present in the reactant acetic acid as well as that produced in the reaction (Faith, et al., 1965).

Typical Cost of Steam Stripping

A process design and cost estimate have been completed for the process shown in Figure 2. The vapor-liquid equilibrium data of Weller, et al. (1963) were used to estimate the relative volatilities in the stripping column. The capital and operating costs were determined as described in Appendix A. The following assumptions were made to define the process:

1. Feed water contains 0.6% n-butyl acetate.
2. Product water contains 50 ppm n-butyl acetate.
3. Feed water flow rate is 100 GPM.
4. Feed water temperature is 80°F.
5. The temperature at the bottom of the column is 230°F.
6. The amount of stripping steam injected directly is that needed to saturate the subcooled feed plus 1.4 times the additional amount needed at minimum flow. The flow of vapor decreases substantially at the feed stage.
7. The distillate is condensed and cooled to 180°F before phase separation occurs.
8. Overall stripping stage efficiency is 75%.

The results of the material balance and the operating conditions are given in Table 1; in Table 2

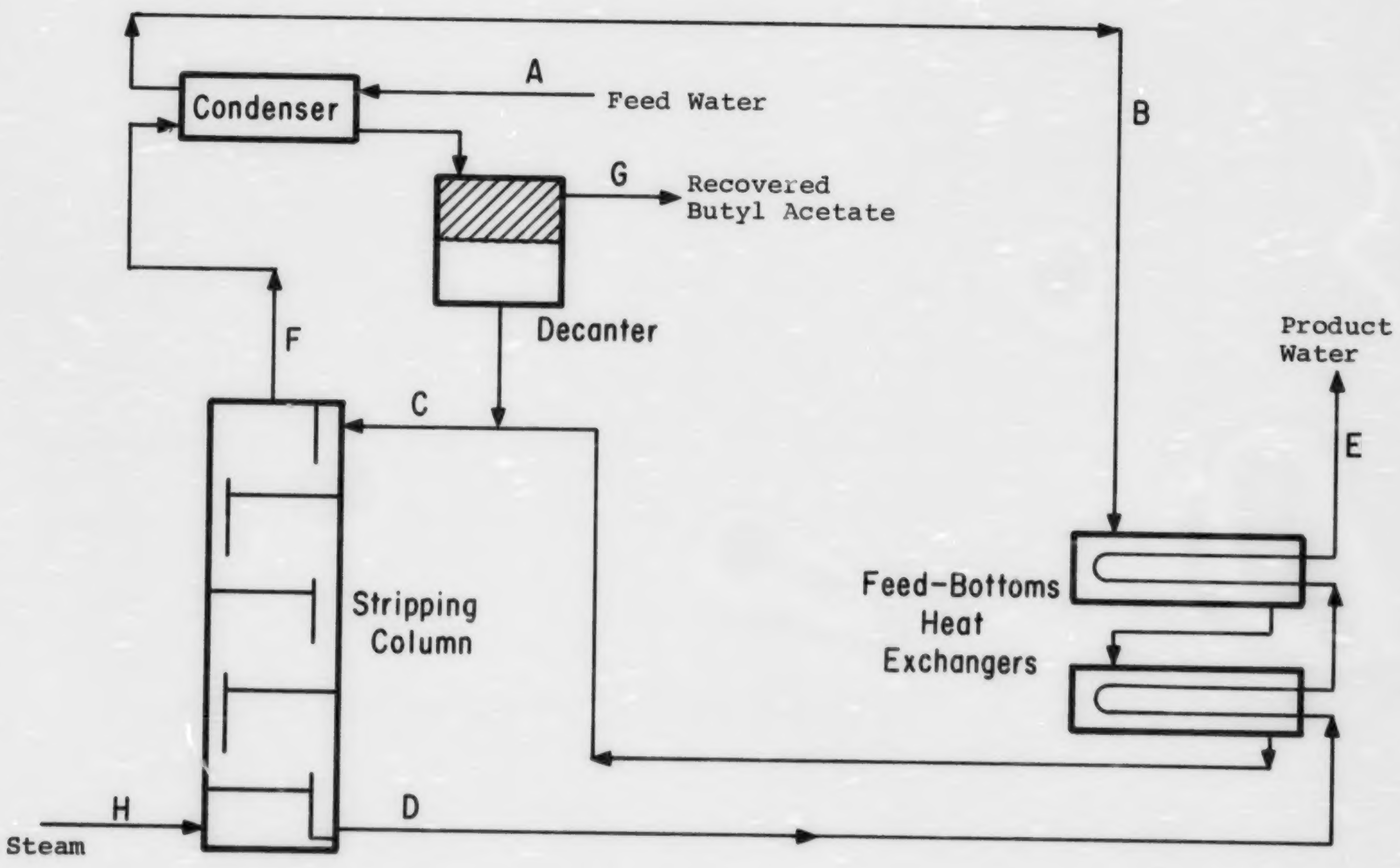


Figure 2. Steam Stripping Process

Table 1. Material Balance for n-Butyl Acetate Recovery by Steam Stripping

Stream (Figure 2)	A	B	C	D	E	F	G	H
Temperature (°F)	80	88	180	230	143	218	180	230
Condition	Liq.	Liq.	Liq.	Liq.	Liq.	Vap.	Liq.	Vap.
n-Butyl Acetate (lb/min)	4.96	4.96	5.04	0.04	0.04	5.00	4.92	0.00
Water (lb/min)	826.6	826.6	832.4	874.8	874.8	6.1	0.3	48.5

Table 2. Cost Estimates for n-Butyl Acetate Recovery by Steam Stripping

Capital Costs:

Total Plant Investment = $41,700

Equipment Item	Percent of Plant Investment
Stripping Column	23
Condenser	4
Decanter	4
Feed-Bottoms Exchangers	69

Operating Costs:

Treatment Cost = $0.61/1000 gal.

Cost Item	$/year
Stripping Steam	18,600
Capital Equipment	10,800

the estimated capital and operating costs are presented. As described in detail in Appendix A, the "Total Plant Investment" includes the cost of all major equipment (stripping column, feed-bottoms exchangers, condenser, and decanter), all auxiliary equipment (piping, concrete, instruments, etc.), labor for material erection and equipment installation, indirect items (freight, construction overhead, engineering, etc.), and an 18% factor for contingency plus contractor's fee. Costs for site development, off-site investment, and working capital are not included. The "Treatment Cost" includes utilities, maintenance, supplies, depreciation, insurance, taxes, and an 8% return on investment. As discussed in Appendix A, the cost of operating labor and laboratory charges have not been included.

For this steam stripping process, the principal cost is associated with increasing the temperature of the entire stream to 230°F. About 69% of the investment is for the feed-bottoms exchangers, and 87% of the stripping steam is that required to increase the temperature of the feed water stream from the feed-bottom exchanger outlet temperature up to its bubble point. The overall operating cost, $0.61/thousand gallons, compares favorably with the value of the recovered n-butyl acetate, $7.40/thousand gallons.

It is well known that low stage efficiencies can occur for systems which have a large relative volatility (Fair, 1973), and in this case the relative volatility ranges from 170 to 200. If the overall stripping stage efficiency were 20% instead of

75% as assumed above, the overall operating cost would increase to $0.69/thousand gallons, and the total plant investment would increase to $55,200 with the stripping column contributing 42% of this total.

Considerations Pertaining to Solvent Extraction.

In contrast to steam stripping, solvent extraction is not considered a general purpose waste treatment process. The usual approach is to choose a specific solvent for use in treating each individual waste water. For example, Kiezyk and MacKay (1973) screened 26 solvents for the single application of treating phenol-containing waste waters. What is needed is a more universal solvent. If this solvent is selected to eliminate the need for recovery of the solvent which is dissolved in the purified water and to make the method of solvent regeneration a clear choice (e.g., distillation), then the difficulty in synthesizing a new process is greatly reduced. This approach was taken in this research to try to develop solvent extraction into a general purpose waste water treatment process.

The bases for solvent selection in the more common solvent extraction separations (Treybal, 1963) do not always apply in waste water extraction. The distribution coefficient, K_d (= ppm pollutant in solvent/ppm pollutant in water), is the most important consideration in choosing a solvent. Since solute concentrations in the waste water are usually in the range from 2% in the feed water down to 10 ppm in the purified waste water, using the value of K_d at infinite dilution, K_d^{∞}, for each pollutant independently is usually satisfactory. Even in cases where K_d is significantly different from its value at infinite dilution, it may still be valid to analyze a process using only K_d^{∞}. K_d directly affects the required ratio of solvent mass flow rate to water mass flow rate, F_s/F_w, through the extraction factor, E (= K_dF_s/F_w). Since E should equal 2 or larger for a practical process giving a high extraction efficiency, a large value of K_d allows efficient pollutant removal at a low value of F_s/F_w. A large value of K_d also allows efficient extraction with a less thoroughly regenerated solvent. The driving force for mass transfer of pollutant from the water into the solvent (which would be used with an overall water-phase mass transfer coefficient) is given by the following relationship between K_d and the bulk concentrations of pollutant:

$$\text{driving force} = \text{ppm in water} - \frac{\text{ppm in solvent}}{K_d}$$

At the solvent inlet end of a counter-current extractor, the concentration of pollutant in the purified water will likely be 10 - 100 ppm. If K_d = 1000, then the regenerated solvent could contain up to 1% pollutant. However, if K_d = 1, then the regenerated solvent must contain less than 10 ppm pollutant. If the solvent is more volatile than the pollutant and if solvent regeneration is carried out by distillation, then rectification will be required to produce this pure a solvent.

Although K_d is very important in solvent selection, it is also a function of the particular pollutant under consideration. Other factors that are not so dependent on the pollutant will have more influence on the choice of a universal solvent. The solvent should be highly insoluble in water to eliminate the need for recovery of the solvent dissolved in the purified water. The information in Table 3 illustrates the importance of solvent solubility for a number of potential solvents. These data indicate that the paraffinic, olefinic, and higher aromatic hydrocarbons may be suitable for a general purpose process.

The solvent should be chosen to have a density much different from that of water so that countercurrent flow or settling in a mixer-settler will proceed easily. All the solvents in Table 3 have a density less than 0.9 gm/cc, except ethylene dichloride which has a density of 1.26 gm/cc. For some pollutants the density difference between solvent and water may decrease significantly as the concentration of pollutant in the solvent increases.

Distillation is the most common method for separating the pollutant from the loaded solvent. If we limit consideration to distillation as a method for solvent regeneration, then the normal boiling point of the solvent is another important property. We could consider a solvent, such as a higher aromatic, with a boiling point above that of the pollutant so that the pollutant would be recovered as a distillate. The major advantage of this mode of operation is the

Table 3. Solvent Solubility Losses

Solvent	Water Solubility (% at 20°C)	Market Price[a] (cents/lb)	Loss[b] ($/1000 gal)
Methyl Isobutyl Ketone	1.9[c]	15½	24.50
Isopropyl Ether	1.2[c]	11½	11.50
n-Butyl Acetate	0.68[c]	15	8.50
n-Hexanol	0.58[c]	12½	6.00
Ethylene Dichloride	0.81[c]	9	6.00
Benzene	0.17[d]	9	1.25
Toluene	0.06[d]	8	0.40
Isobutylene	0.053[e]	6	0.26
Xylenes	0.02[d]	7	0.12
Isobutane	0.015[d]	4	0.05
n-Hexane	0.001[d]	8	0.0[illegible]

[a] Data from Chemical Marketing Reporter (March 25, 1974).

[b] Assuming no solvent entrainment.

[c] Data from Union Carbide (1973).

[d] Data from API (1963).

[e] Estimated from Matsuura and Sourirajan (19

elimination of the need to boil the entire solvent recycle stream. However, a major disadvantage is the accumulation of high boiling impurities from the waste stream. These impurities would be expected to change K_d and the physical properties of the solvent. The other alternative is to choose a solvent with a much lower boiling point than the pollutant. We will refer to this option as volatile solvent extraction.

Choice of Volatile Solvent.

Consider the C_3 to C_6 paraffinic and olefinic hydrocarbons as possible universal solvents. Such a volatile solvent process would probably be arranged as in Figure 3 (shown for isobutylene as the volatile solvent). The pressure in the extractor will be slightly above the vapor pressure of pure solvent (to avoid vaporization due to temperature fluctuation) at the extractor temperature. The pressure in the distillation column will be determined by the temperature in the condenser. To avoid refrigeration and to use cooling water, the condensation temperature should be about 110°F or higher. These factors make the C_6 hydrocarbons the favored choice. However, the volatility of the solvent relative to the pollutant should be large to make the distillation easy. This factor makes the C_3 hydrocarbons appear better. A compromise is necessary in the choice of best solvent, as is illustrated by the following approximate calculations.

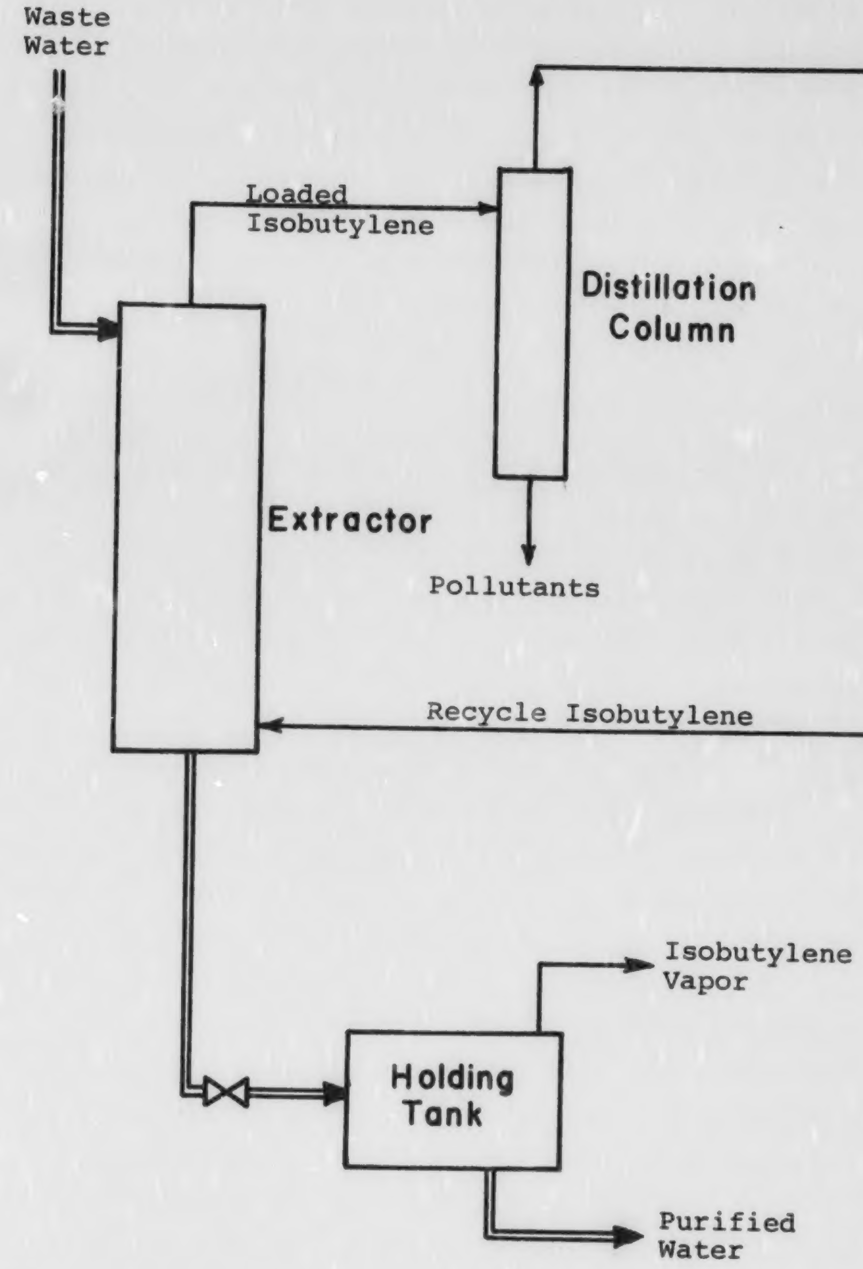


Figure 3. Typical Volatile Solvent Process

For the case where a hydrocarbon solvent extraction is used to recover dissolved ethylene dichloride from a waste water, we will assume that binary liquid mixtures of ethylene dichloride and each hydrocarbon behave as regular solutions (Hildebrand, et al., 1970). Won (1973) has determined the distribution coefficient for ethylene dichloride between water and isobutylene to be about 70. In dilute solutions the distribution coefficient, K_d, is related to the activity coefficients of ethylene dichloride in the water, $\gamma_{EDC}^{(H_2O)}$, and in the hydrocarbon, $\gamma_{EDC}^{(HC)}$, and to the molecular weights of water and hydrocarbon, MW_{H_2O} and MW_{HC}, as follows:

$$K_d = \frac{MW_{H_2O}}{MW_{HC}} \cdot \frac{\gamma_{EDC}^{(H_2O)}}{\gamma_{EDC}^{(HC)}}$$

For isobutylene, we calculate $\gamma_{EDC}^{(HC)}$ from the regular solution theory by neglecting the effect of water in the hydrocarbon phase. This allows $\gamma_{EDC}^{(H_2O)}$ to be calculated using the experimental value for K_d. We assume that $\gamma_{EDC}^{(H_2O)}$ does not change from hydrocarbon solvent to hydrocarbon solvent. Therefore, K_d for each solvent may be determined by again applying regular solution theory. The results of this estimation are shown in the first column of Table 4 for a series of hydrocarbons from C_3 to C_6. Solubility parameters and molar volumes were taken from Chao and Seader (1961).

Also for the purpose of illustrating trends, the Chao-Seader (1961) estimation method may

Table 4. Factors Affecting Solvent Choice

Hydrocarbon Solvent	K_d	Column Pressure (psia)	Distillate Temperature (°F)	Relative Volatility (when $X_{EDC}=0$)	Bottoms Temperature (°F)	Relative Volatility (when $X_{EDC}=0.97$)
Propane	65	212	110	8.3	347	16.8
Propylene	70	253	110	9.2	367	14.8
n-Butane	66	60	110	4.4	247	18.8
i-Butane	66	83	110	5.8	269	19.6
1-Butene	70	72	110	5.1	262	17.5
i-Butylene	70	74	110	5.4	263	17.6
n-Pentane	67	19	110	2.0	183	11.9
1-Pentene	70	23	110	2.9	193	13.7
n-Hexane	67	17	164	0.78	188	4.5
1-Hexene	68	17	155	0.99	187	5.3

be used to calculate the relative volatilities of mixtures of hydrocarbons and other non-polar compounds (assumed to include ethylene dichloride). It is assumed that the solvent regeneration column will operate at slightly above atmospheric pressure or at a higher pressure if that is necessary to condense the distillate at 110°F using cooling water. Thus fixing the column pressure, the volatility of solvent relative to ethylene dichloride is calculated at a point approaching pure solvent (i.e., like the distillate composition) and at a point where the mole fraction of ethylene dichloride is 0.97 (i.e., like the recovered pollutant product composition). These values are also included in Table 4 along with the distillate and bottom product bubble point temperatures.

If we compare the estimated distribution coefficients for the C_3 to C_6 hydrocarbons, we see that there are no significant differences except that the olefins are slightly better solvents than the paraffins. Experimental differences between olefins and paraffins are somewhat larger (Won and Prausnitz, 1974), but the olefins, being more reactive, can not always be considered (e.g., for treating acidic waste waters). Comparing the C_3 and C_4 hydrocarbons shows that the relative volatility favors the C_3's and the operating pressure favors the C_4's. However, the relative volatility of 4 to 6 for the C_4's should be large enough to make the separation easily, so the C_4's are the better choice. The C_6 hydrocarbons are good in terms of low pressure and high distillate temperature (requiring a smaller condenser), but the relative volatility is too small, even forming azeotropes. The choice between the C_4 and C_5 hydrocarbons is not as clearly indicated, but the slight increase in cost to operate the column at 60 to 83 psia should be smaller than the cost associated with the more difficult separation in the upper portion of the column in the case of the C_5's. Also, the C_4 hydrocarbons are generally more readily available. On the basis of this simple comparison, we chose to study the C_4 hydrocarbons, isobutylene and isobutane. The iso- rather than the normal-isomers were chosen because they are less soluble in water. An even more readily available solvent would be a mixture of these C_4 paraffins and olefins.

Considerations in Volatile Solvent Extraction.

Many of the factors discussed previously for a general solvent extraction process also apply to volatile solvent extraction. These factors can be illustrated by estimating the costs of treating a typical waste water. For this purpose, we will consider the recovery of ethylene dichloride from a water solution using isobutylene as the volatile solvent. This pollutant occurs in the waste waters from the production of vinyl chloride and is non-biodegradable.

The loaded solvent from the extractor is a dilute, subcooled liquid consisting of a wide-boiling mixture. During the distillation, all the volatile solvent must be boiled and then condensed making heat economy very important. If the loaded solvent is added directly to a simple distillation column having a single reboiler, then all the heat required to vaporize the solvent must be supplied at the temperature of the reboiler. From Table 4, if the distillation column were operated at 74 psia using cooling water for condensing, then the reboiler will operate at 263°F. As is discussed in detail in Appendix D, other alternatives result in a much lower cost for solvent regeneration.

One alternative which substantially reduces the regeneration cost utilizes a total feed vaporization. In this alternative most of the heat to boil the solvent can be supplied at a lower temperature using exhaust steam. However, more reflux is required than for a subcooled liquid feed resulting in larger amounts of heat supplied and removed.

A second alternative, which is better than either of the above two, utilizes a subcooled liquid feed; however, several stages below the feed point the downflowing liquid is drawn off and partially vaporized. The exact location of this side stream boiler is subject to optimization, but it is chosen so that the temperature of the boiler is low enough to be driven with exhaust steam. With ethylene dichloride the optimum location results in a side stream boiler temperature of about 128°F. This last alternative allows supply of most of the heat using exhaust steam but does not increase the amount of reflux over that required for a subcooled liquid feed. Other savings such as a lower cost for the distillation column are described in Appendix D.

A practical mode of operation of the distillation column condenses the distillate at 120°F, uses a vapor flow in the portion of the column below the side boiler 20% above minimum vapor flow, and locates the side stream boiler several stages below the feed point. This alternative is particularly attractive when the relative volatility is low at a high concentration of pollutant, as is the case with phenol in n-butyl acetate.

The distribution coefficient for the extraction of ethylene dichloride with isobutylene is about 70. Therefore, the volatile solvent extraction process can be operated with a solvent-to-water flow ratio of 1:30 and still have the extraction factor large enough for efficient pollutant removal. At these low solvent flow rates, the heat released in the condenser is small enough that the purified waste water can be used as coolant rather than using cooling water. This reduces the operating cost for cooling water, but in all the alternatives the condenser represents a substantial capital cost. This cost can also be reduced through the use of a direct contact condenser.

Direct contact condensation has seen infrequent use in industry. It was studied by Harriott and Wiegandt (1964) in conjunction with a desalination process. These authors measured volumetric heat transfer coefficients for the condensation of methylene chloride with water in a packed bed and on a single sieve plate. Their data can readily be used to estimate the design of a direct contact condenser using the cool purified waste water to condense the overhead vapors (isobutylene) from the distillation column.

For cost estimation purposes, we consider a short, packed bed with the purified waste water being distributed on top of the packing and the vapors entering from below. Both the condensed organic and the water flow out the bottom of this device as a two-phase mixture and are settled in a separate tank. Other types of contacting devices could also be used and are expected to result in comparable costs; they may be preferred if suspended solids are present. Devices which allow vapors to condense on a film of water should eliminate a potential problem in which the small condensed organic droplets could form a stable emulsion in the purified water.

Since the purified waste water leaving the extractor is already saturated with volatile solvent, its direct contact with the distillate will not result in additional pollutants being added to the purified water. In fact, the direct contact condenser will act as an additional extraction stage (at a higher temperature where K_d is usually lower). This arrangement of the volatile solvent process is shown in Figure 4. The quantitative effects of replacing the normal condenser by a direct contact condenser on the operation and cost of the process are discussed below.

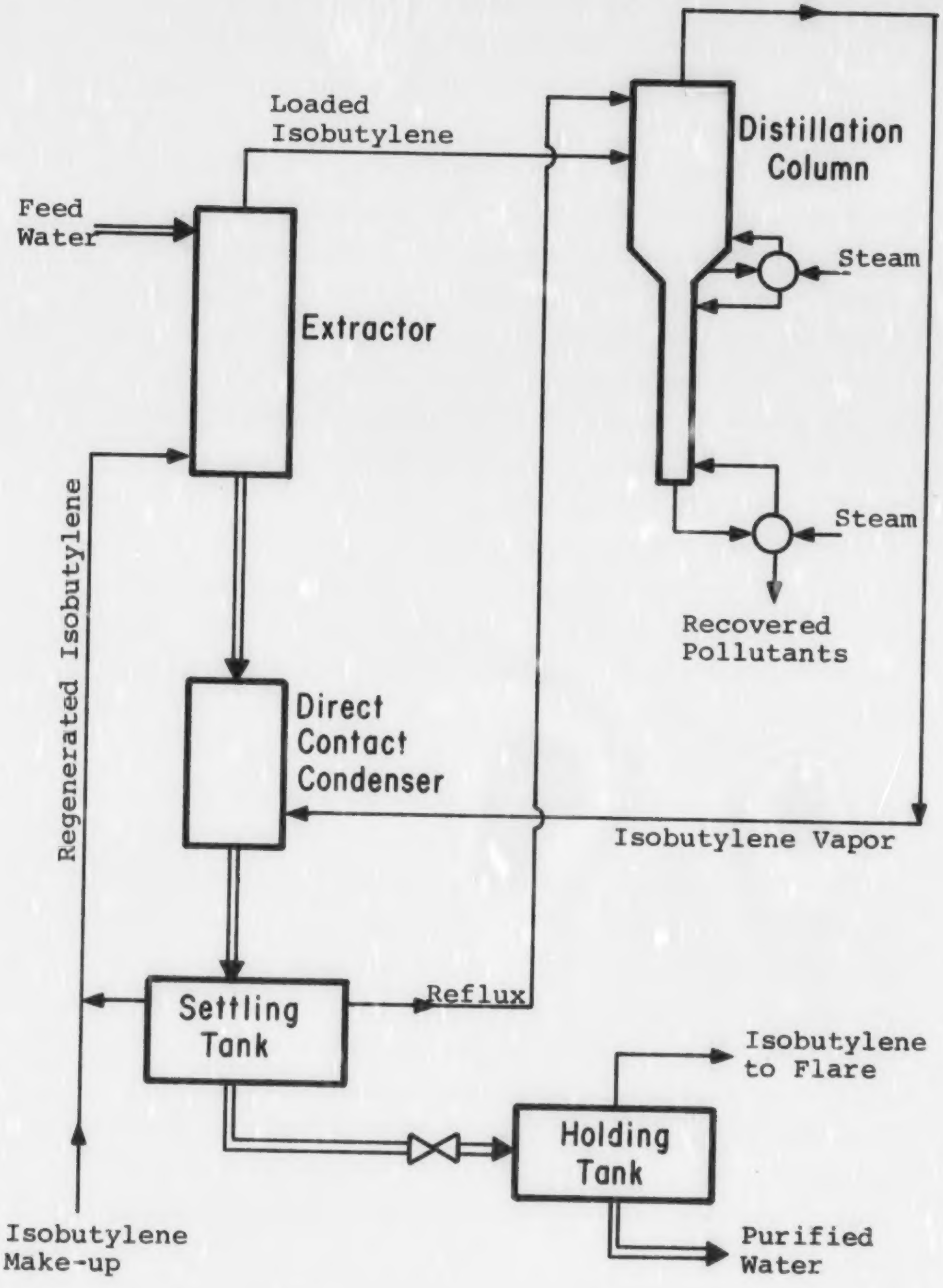


Figure 4. Detailed Volatile Solvent Process

The substantial cost of regenerating the solvent and the opportunity to use a direct contact condenser clearly favor operation with as low a solvent-to-water flow ratio, F_s/F_w, as possible. The lower limit is determined at the point where the extraction factor, E (= K_dF_s/F_w), becomes so low that the cost of the extractor offsets the savings in volatile solvent regeneration. For pollutants having a large K_d (i.e., greater than 30), the optimum F_s/F_w will likely be 0.1 or less. However, not all types of extraction equipment will operate efficiently at such low values of F_s/F_w. Mixer-settlers can operate well since settled solvent can be recycled to the previous mixer without destroying the counter-current operation, but these devices are very expensive if many extraction stages are required. The rotating disc contactor (RDC) has been used successfully with a low flow ratio (Misek and Rozkos, 1966). The design of an RDC without detailed mass transfer data is only approximate, and therefore for preliminary estimates of cost a mixer-settler will be used.

Typical Cost of Volatile Solvent Extraction.

A preliminary cost evaluation has been completed for the recovery of ethylene dichloride (EDC) from a waste water by extraction with isobutylene. The following assumptions were made:

1. Feed water contains 0.8% EDC.
2. Extraction removal efficiency is 95%.
3. Feed water flow rate is 100 GPM.

4. Feed water temperature is 80°F.
5. Recovered EDC residue contains 1.5 wt. % isobutylene.
6. Regenerated solvent contains 0.56 wt. % EDC. This will reduce the driving force at the water outlet of the extractor by 20% from that if a pure solvent had been used.
7. Distillate is condensed at 120°F using cooling water which is heated from 80°F to 100°F, or using direct contact condenser when possible to do so without heating the purified water above 100°F.
8. Distillation column operates as described in Appendix D with a 75% Murphree vapor stage efficiency.
9. 10-minute liquid hold-up is used in both water and reflux tanks.
10. 3-minute liquid hold-up is used in the bottom of the distillation column.
11. A multiple-stage mixer-settler is used for extraction with a solvent recycle, if necessary to give a volumetric ratio of 0.6 ft^3 solvent per ft^3 water, and a stage efficiency of 85%. Mixer-settler costs are estimated from the data of Treybal (1963).

Based on these assumptions using $K_d = 70.0$ and estimating vapor liquid equilibria from the Chao-Seader correlation, costs were estimated for F_s/F_w from 0.08 to 1.5 using the methods of Appendix A. The distribution of capital costs is shown in Table 5 for the two extremes of F_s/F_w.

Table 5. Capital Costs for EDC Recovery

Capital Cost	$F_s/F_w=0.08$	$F_s/F_w=1.50$
Total Plant Investment	$108,700	$156,100

Equipment Item	Percent of Total	
Distillation Column	12	12
Condenser	3*	29
Side Stream Boiler	2	20
Reboiler	1	1
Tanks	5	8
Pumps	9	7
Extractor	68	23

* Direct contact condenser + settling tank

For the low flow ratio, the major capital cost item is the extractor. For the high flow ratio, the major capital cost is associated with heat exchangers to vaporize and condense the volatile solvent.

The operating costs for this volatile solvent extraction process are divided into an amortized capital cost for the extractor (including a prorated portion of maintenance, repairs, supplies, depreciation, insurance, taxes, and return on investment) and a cost associated with all other items (including the remaining portion of the above capital related costs plus chemicals and utilities, but not including operating labor and laboratory costs). Figure 5 shows such a division of costs for ethylene dichloride extraction and illustrates the advantages of operating at a low flow ratio. The discontinuities in the curve for the mixer-settler result from a requirement for abrupt increases in the number of stages to achieve at least 95% recovery as the flow ratio decreases. The discontinuity in the curve for "other" costs results from the use of purified waste water for cooling instead of cooling water and the use of a direct contact condenser. Figure 6 shows a breakdown of the regeneration costs. For comparison, the recovered EDC is estimated to be worth $5.70/thousand gallons at its full market value.

At values of $F_s/F_w = 0.135$ and less, the purified waste water can be used to condense all the distillate vapors, making the direct contact condenser practical. The reduction in cost when

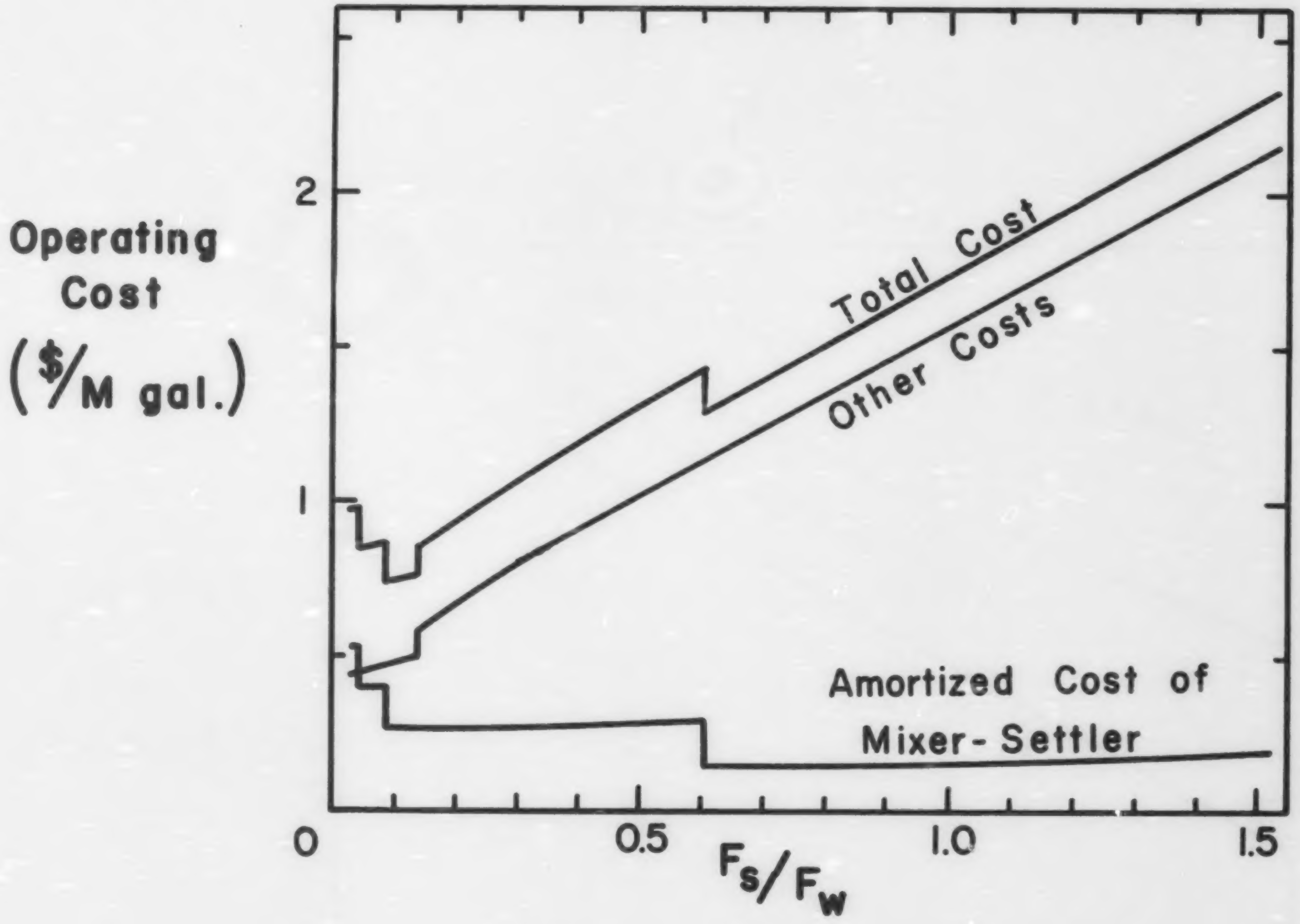


Figure 5. Total Cost of EDC Recovery

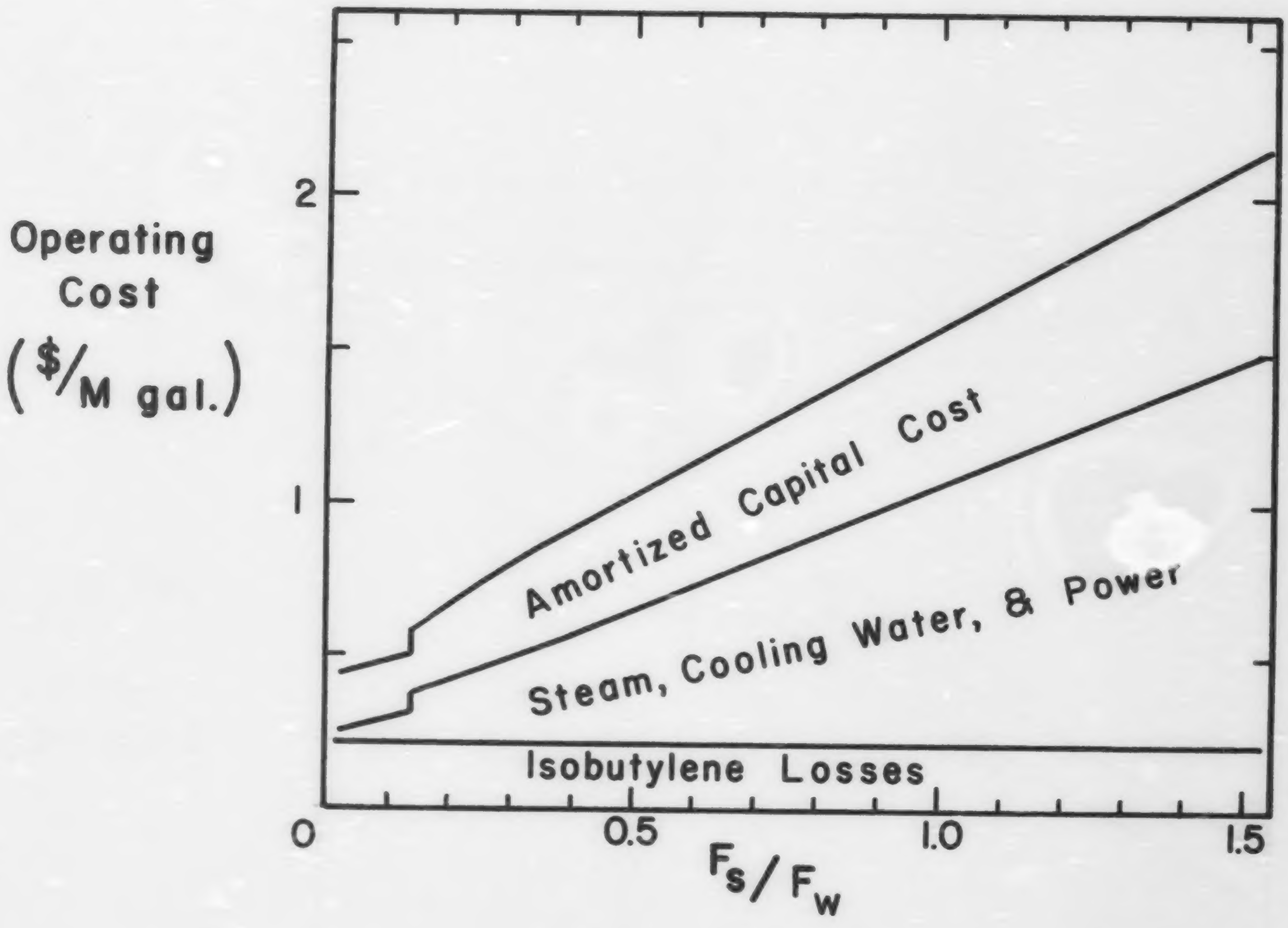


Figure 6. Breakdown of Costs for EDC Recovery (Excluding Extractor)

using the direct contact condenser is greater than just the reduction in cooling water and condenser cost. The volumetric heat transfer coefficient is so large (i.e., about 50,000 BTU/hr ft^3 °F) that the optimum distillate temperature is reduced to about 1° above the final temperature of the purified waste water. This results in a reduction in pressure within the distillation column and a reduction in cost for the solvent recycle pump, for the distillation column (through both a higher relative volatility and a smaller shell thickness), and for both boilers (through an increase in temperature driving force). There is a slight increase in cost due to a larger feed water pump and operation of the extractor at higher pressure.

Figure 5 can be used to determine a first-order approximation to the costs of extracting other pollutants. The cost of solvent regeneration depends primarily on F_s/F_w for any pollutant with a volatility similar to that of ethylene dichloride. The cost of extraction depends primarily on K_d and on the required removal efficiency. Therefore, for 95% removal efficiency, the curve for extractor costs can be moved horizontally to a point giving the same cost vs. E as in Figure 5 (where K_d = 70.0). If K_d is less than 70.0, the curve would be moved to the right to provide an estimate for extractor costs. This argument leads to the conclusion that the optimum F_s/F_w will increase as K_d decreases.

Comparison of Volatile Solvent Extraction with Steam Stripping.

For very volatile pollutants having a low K_d with the volatile solvent, steam stripping is expected to be less expensive than volatile solvent extraction. As higher molecular weight pollutants are considered, extraction is more competitive. This is especially true if the pollutant is present as an emulsion, if the pollutant forms an azeotrope with a high fraction of water, or if the waste water would become highly corrosive at increased temperatures. However, the cost of volatile solvent extraction can be comparable to or less than steam stripping even when the latter is known to be a practical process.

A process design and cost estimate have been completed for a process in which isobutylene is used to extract n-butyl acetate (Figure 7). The distribution coefficient for n-butyl acetate into isobutylene is 168 (Appendix E). The assumptions about water flow rate, feed and product concentrations, and feed water temperature are the same as those for the previously described cost estimate for the recovery of n-butyl acetate by steam stripping. The recovered n-butyl acetate was assumed to contain 2.0 wt. % isobutylene, and the regenerated solvent was assumed to contain 0.168 wt. % n-butyl acetate (based on a driving force at the water outlet of the extractor 20% less than the driving force if pure isobutylene had been used).

A direct contact condenser is used since the optimum F_s/F_w is 0.11 (requiring 2 mixer-settler stages). Table 6 gives the material balance and operating conditions for the conceptual process, and Table 7 presents the cost estimates. The cost for volatile solvent extraction is $0.71 per thousand gallons as compared to $0.61 per thousand gallons for steam stripping.

Realizing the approximate nature of the estimates, these costs are essentially equal. For the extraction process a majority of the cost is associated with the extractor, the cost of which might be reduced by using a different type of contactor (e.g., an RDC). Also, the assumption of a 75% stage efficiency for both steam stripping (where the relative volatility ranges from 170 to 200) and for n-butyl acetate-isobutylene distillation (where the relative volatility ranges from 15 to 54) is probably optimistic in both cases, but certainly is more likely to be correct when the relative volatility is lower. Considering these factors, volatile solvent extraction does appear to be an economically attractive alternative to steam stripping.

To estimate the cost of extracting ethylene dichloride, n-butyl acetate, or other potential pollutants, it is necessary to have available estimates for K_d and for the binary vapor-liquid equilibria between pollutant and volatile solvent. Appendix E reports values for K_d at high dilution between water and C_4 hydrocarbons for a variety of esters, aldehydes, ketones, and phenols. For relatively non-polar polutants (e.g., ethylene

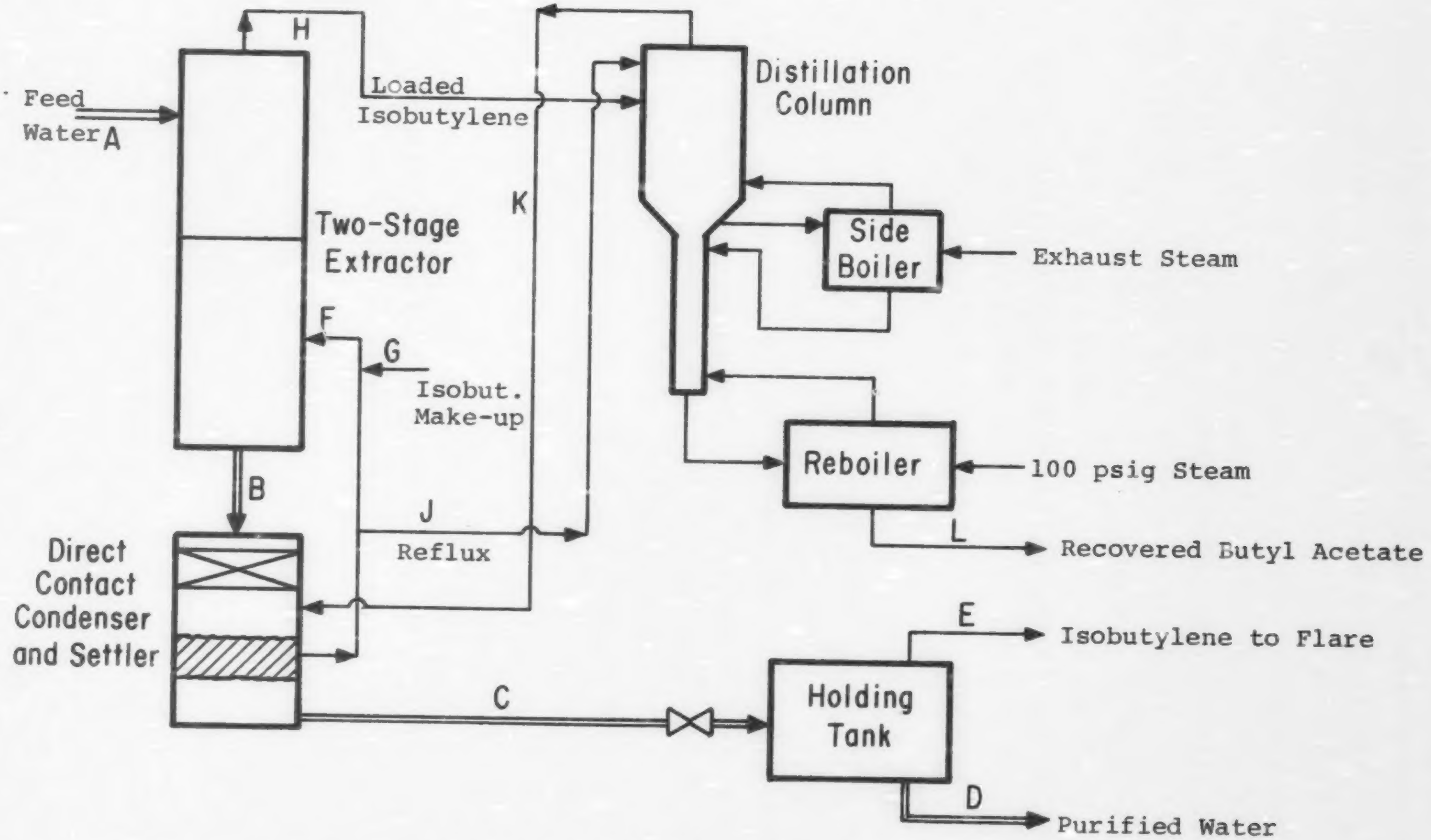


Figure 7. Details of Volatile Solvent Extraction Process

Table 6. Material Balance for n-Butyl Acetate Recovery by Solvent Extraction

Stream	A	B	C	D	E	F	G	H	J	K	L
Temperature (°F)	80	80	96	96	96	97	80	80	97	97	330
Pressure (psia)	58	57	57	15	15	57	57	58	58	58	58
Condition	liq.	liq.	liq.	liq.	vap.	liq.	liq.	liq.	liq.	vap.	liq.
Water (lb/min)	826.6	826.6	826.6	826.6	≈0	≈0	≈0	≈0	≈0	≈0	≈0
Isobutylene (lb/min)	0	0.5	0.5	0.2	0.3	91.3	0.6	90.8	4.5	95.2	0.1
Butyl Acetate (lb/min)	4.96	0.04	0.04	0.04	0	0.15	0	5.07	0.01	0.16	4.92

Table 7. Cost Estimates for n-Butyl Acetate Recovery by Solvent Extraction

Capital Costs:

Total Plant Investment = $78,600

Cost Item	Percent of Total
Extractor	63
Distillation Column	11
Direct Contact Condenser and Settler	5
Side Stream Boiler	1
Reboiler	1
Tanks	8
Pumps	11

Operating Costs:

Total Treatment Cost = $0.71/1000 gal.

Cost Item	Annual Cost
Chemicals	$10,100/yr
Utilities	3,500/yr
Capital Equipment	20,300/yr

dichloride), vapor-liquid equilibria can be estimated using the Chao-Seader correlation (1961). This approach is based on regular solution theory for prediction of liquid activity coefficients and is not reliable for polar components. However, an alternative approach based on the Wilson equation (1964) for liquid activity coefficients should give reliable estimates.

For a binary solution, the Wilson equation has two adjustable parameters and is of a form which allows the effect of temperature on the activity coefficients to be estimated. This is an important feature since at constant pressure the temperature varies over a wide range with composition for a mixture of a volatile solvent and a much-less-volatile pollutant. The two Wilson parameters may be evaluated by a simple iterative calculation using the two infinite dilution activity coefficients. The infinite dilution activity coefficient for the pollutant in the volatile solvent may be estimated for many pollutants from K_d at 25°C and the activity coefficient at infinite dilution for the pollutant in water (Pierotti, et al., 1959). The infinite dilution activity coefficient for the volatile solvent in the pollutant at 25°C may be estimated by the method of Helpinstill and Van Winkle (1968) or the method of Weimer and Prausnitz (1965). Vapor phase nonidealities can adequately be approximated using the Redlich-Kwong equation of state, as is done in the Chao-Seader method. This procedure was used in the estimation of vapor-liquid equilibria for the separation of n-butyl acetate from isobutylene. The procedure may also be extended to multicomponent mixtures when more than one pollutant is extracted, provided some estimate can be made for the pollutant-pollutant binary mixtures.

Dual Solvent Extraction Processes.

The attractiveness of volatile solvent extraction for the recovery of n-butyl acetate, a known good solvent for phenol extraction (Kiezyk and MacKay, 1973) leads to the consideration of a dual solvent extraction process for the recovery of phenol. Such a process is illustrated in Figure 8. The phenol is removed from the waste water by extraction with n-butyl acetate (K_d = 57; Appendix F) at a low flow ratio. The phenol is separated from n-butyl acetate by distillation as was done in the original Phenolsolvan process (Wurm, 1968). The dephenolized water contains about 6800 ppm dissolved n-butyl acetate, which is recovered by extraction with isobutylene. The recovered n-butyl acetate is separated from the isobutylene by distillation and is recycled to the n-butyl acetate solvent cycle. Other polar solvents could also be considered for such a dual solvent process, with the best choice being a solvent which is easily recovered by volatile solvent extraction as well as being a good solvent for phenol.

An alternative dual solvent process is shown in Figure 9, where the phenolic waste water is first extracted with a mixture of volatile solvent and n-butyl acetate, and then the volatile solvent is used to recover the dissolved n-butyl acetate.

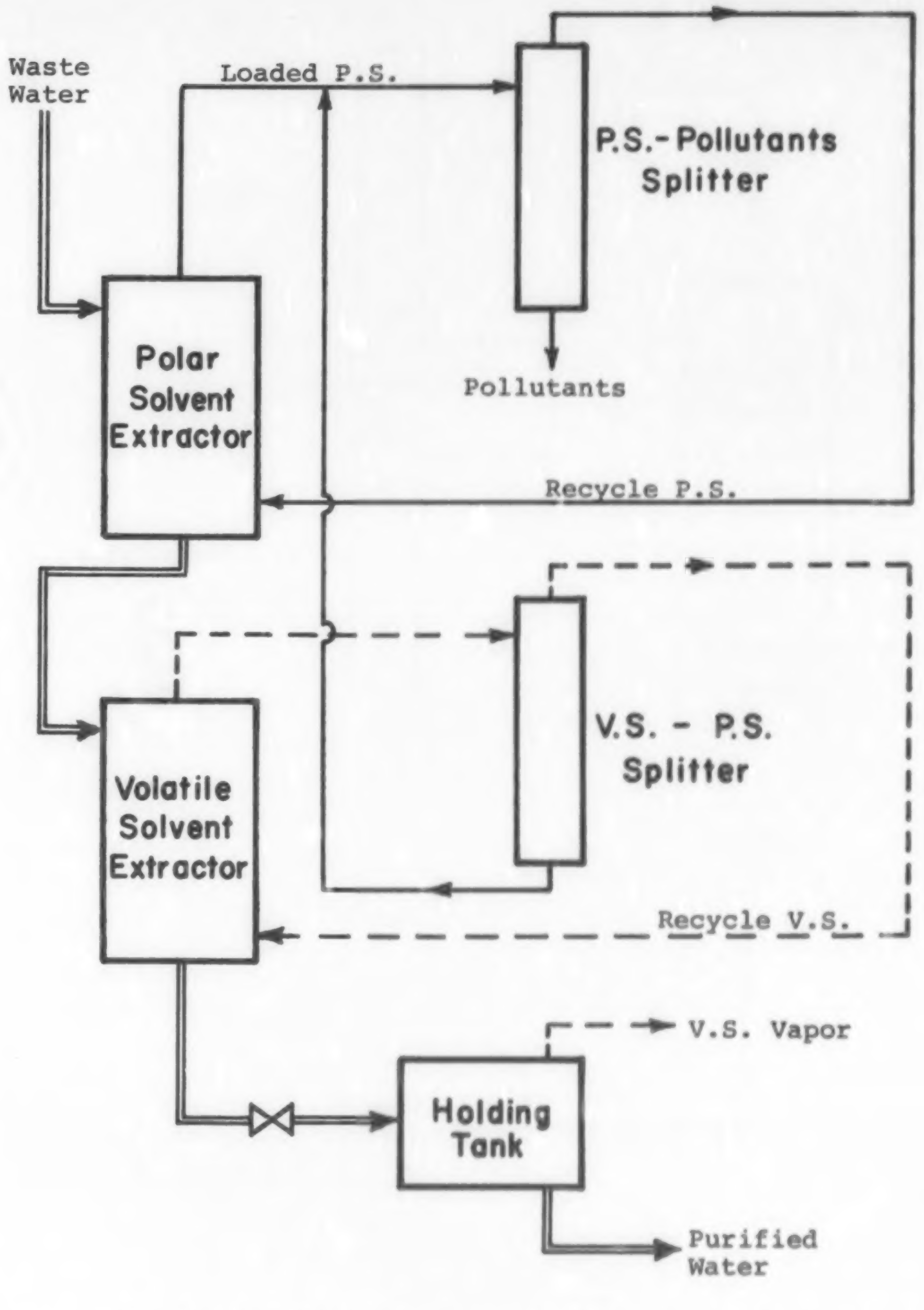


Figure 8. Dual Solvent Process (Separate Solvent Cycles)

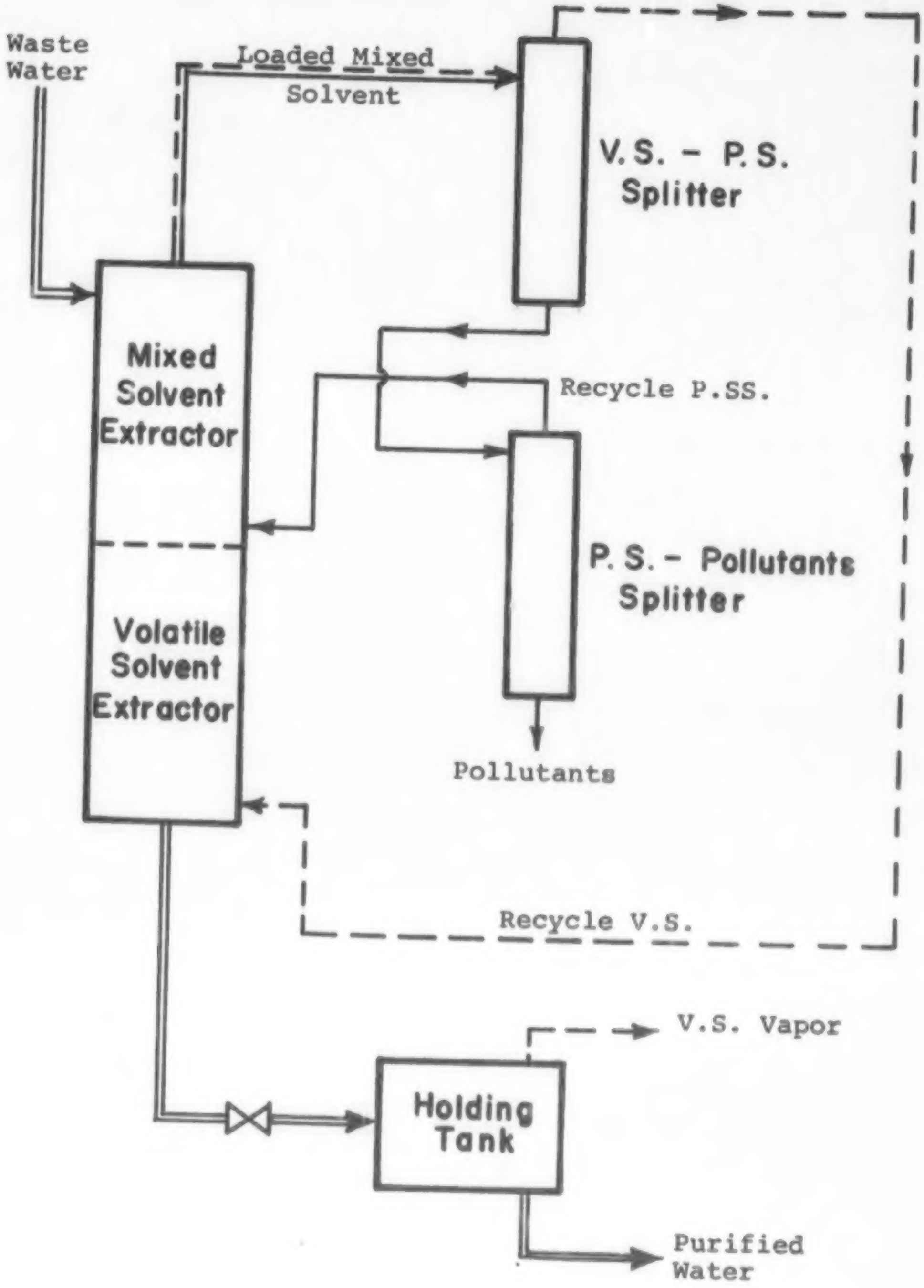


Figure 9. Dual Solvent Process (Linked Solvent Cycles)

This process with linked solvent cycles has several potential advantages over the dual solvent process with separate solvent cycles while still requiring only two distillation columns. For extraction with pure n-butyl acetate, the density of phenol-containing solvent becomes close to that of water. This small density difference leads to large extraction equipment because of slow settling in mixer-settlers or low countercurrent flows to avoid flooding in continuous extractors. However, dilution of the n-butyl acetate with isobutylene greatly increases the density difference and allows operation in smaller, less expensive extractors. The extraction with a solvent mixture also results in a lower solubility of n-butyl acetate in the dephenolized waste water, thus requiring less thorough volatile solvent extraction in the second step. However, the dual solvent process with separate solvent cycles, Figure 8, has the potential advantage that the hot n-butyl acetate vapors from the phenol-polar solvent splitter may be more easily used to provide heat for the volatile solvent-polar solvent splitter.

Although illustrated for the recovery of phenol, the dual solvent processes may also be attractive for other pollutants. The conditions when a second polar solvent should be considered are a low K_d (e.g., less than 5) for the pollutant in the volatile solvent and a high K_d (e.g., greater than 20) for the pollutant in a polar solvent. Almost all slightly soluble polar solvents will show a high K_d in the volatile solvent because the same factor leading to low water solubility (i.e., a high activity coefficient in water) also leads to a high K_d.

The examination of both single volatile solvent extraction and alternative dual solvent extraction processes constitutes the major portion of the experimental work to be described in this report.

SECTION V

BASES FOR EXPERIMENTS AND INDUSTRIAL WASTEWATERS EMPLOYED

Experiments were carried out to determine equilibrium distribution coefficients for various important solutes between various solvents and water. Appendix E reports methods and results for various families of compounds using isobutylene, isobutane and other substances as solvents. Appendix F reports distribution coefficients for phenolic solutes with various solvents.

The demonstration program using the miniplant extraction facility consisted of two portions. The first series of experiments was conducted in a spray tower extractor for the purpose of studying the overall process feasibility of volatile solvent extraction. During these experiments volatile solvents were used to treat a variety of actual and synthetic waste waters. The objectives of these initial experiments included (1) the quantitative measurement of pollutant removal efficiencies for both solvent-phase dispersed and aqueous-phase dispersed, (2) the identification of possible solvent degradation reactions when isobutylene was used as solvent, (3) the determination of whether emulsified liquids and particulate solids in actual waste water could be removed through flotation by solvent droplets, and (4) the verification that the loaded solvent could be sufficiently well separated from the pollutants in a short, packed distillation column so that the solvent could be recycled.

During the second portion of the experimental program, a rotating disc contactor (RDC) was used in place of the spray column since the results of earlier experiments and conceptual process calculations had shown that operation with a low solvent-to-water flow ratio (F_s/F_w) would lead to a more economical process. The system of using a C_4 hydrocarbon as solvent is characterized by a low solvent viscosity and a large difference in density between solvent and water. These properties along with a lower limit on the practical size of holes in the distributor plate of a spray column lead to a low dispersed phase hold-up at all values of F_s/F_w when water is dispersed and at low values of F_s/F_w when the solvent is dispersed. A low hold-up and thus a low interfacial area leads to poor extraction efficiency. In an RDC, the dispersed phase hold-up can be increased by increasing the disc rotational speed which results in smaller drops and improved extraction efficiency. Although this is an overly simplified comparison, the result is that the RDC is expected to work satisfactorily even when F_s/F_w is low (e.g., $F_s/F_w = 0.1$) (Misek and Rozkos, 1966). Also the RDC is more characteristic of modern, high-performance types of extractors, so the collection of mass transfer data will be more useful for scale-up and estimation of commercial feasibility. During the second series of experiments, effort was mainly directed toward treating several actual waste waters that we believed to be promising candidates for economical treatment by solvent extraction at low flow ratios.

An important aspect of the experimental approach for actual waste waters involved the identification of the individual pollutants present. To understand, evaluate and improve the solvent extraction process, it was desirable to determine the removal efficiency for each of the identified major pollutants. Seven separate types of waste water samples were obtained from petroleum and chemical companies and were treated in the miniplant.

In this Section the industrial waste waters which we studied are first described with respect to the identification of pollutants and to the logical approach for treatment by solvent extraction. The importance of axial dispersion (backmixing) on the performance of solvent extraction equipment is discussed, and a method of estimating the individual-phase resistances to mass transfer from miniplant data is developed.

Industrial Waste Water Samples

Lube oil refining waste water. One waste water sample came from a lube oil refining plant. This waste water is produced during solvent refining and deasphalting (by the Duo-Sol process) and dewaxing (by MEK-benzene extraction) of lubricating oils in a typical petroleum refinery. The waste waters produced by these operations would be expected to contain phenol and cresols, which are used as a mixed solvent in the Duo-Sol process, and methyl ethyl ketone (MEK) and benzene, which are used as solvents for dewaxing. In addition to the dissolved organic pollutants, the waste water contained a small amount of floating oil and fine, black, solid particles (possibly asphaltenes) which did not settle on standing and which were not removed by filtering with qualitative grade filter paper.

The procedure used to identify the typical pollutants will be described here as it was used with slight modification for all the actual waste waters. A GC analysis (Porapak Q at 200°C) showed that the waste water contained five major dissolved components. By comparing retention times in the GC, four of the five pollutants were tentatively identified as MEK, benzene, phenol, and o-cresol. The fifth component had a retention time similar to that of acetone (which could enter the process as an impurity in MEK). A standard solution was prepared which contained these five components in about the same concentration as the waste water; the pH of this synthetic sample was the same as the actual waste. Equal volumes of the actual and synthetic samples were contacted in a separatory funnel with equal volumes of highly purified n-butyl acetate, and the aqueous raffinates from both extractions were analyzed using the GC. Since the percentage extracted for each of the five peaks was identical for both samples, this was taken as confirmation of the pollutant identification. Had some uncertainty existed at this point, a second comparative extraction using a different solvent could have been used. This simple procedure was useful because the number of expected pollutants was not too large and because their expected identity was known. Had more major pollutants been present or had no estimate been available of what pollutants might be present, then a more sophisticated analysis such as that of Herz (1972) or Sugar and Conway (1968) could have been required.

In addition to the chromatographic analysis, the chemical oxygen demand (COD) was measured by a standard method (described in Section VI). A theoretical COD was determined from the GC analysis by assuming that all identified components were completely oxidized to CO_2 and H_2O. The ratio of theoretical to measured COD averaged 1.10 for the lube oil refining waste water. This indicates that there may have been some loss of volatile components or have been an incomplete oxidation of organics in the measured COD and that there were no components present in large concentration other than those identified by the GC analysis.

Samples of this lube oil refining waste water were obtained on four occasions. The concentration of components in three of these samples fell into the following ranges:

Acetone:	25 to 40 ppm
MEK:	108 to 232 ppm
Benzene:	37 to 170 ppm

Phenol:	17,000 to 23,200 ppm
o-Cresol:	1,200 to 2,660 ppm

This is probably the composition during normal operation. The fourth sample was found to contain a much different composition. Acetone and benzene were absent, MEK was present at about 100 times higher concentration than normal, and phenol and o-cresol were present at about one-half their normal concentrations. In addition, the appearance was milky white rather than black as in the normal samples. This variation in composition was probably the result of an upset in the dewaxing plant. It illustrates another problem not encountered in tests with synthetic waste water samples, that of variation in feed water composition.

Since the major pollutants in this waste water were polar organic compounds which are difficult to extract with hydrocarbon solvents, treatment had to use either volatile solvent extraction at a high value of F_s/F_w or polar solvent extraction as part of a dual solvent process. Both approaches were studied using isobutylene as volatile solvent and n-butyl acetate as polar solvent.

Cresylic acid recovery waste water. The second waste water sample came from a cresylic acid recovery plant which reprocesses the caustic treating effluent produced during petroleum refining. Since caustic treating is used to extract phenolic compounds from petroleum, the waste water was analyzed by GC (Porapak Q at 220°C) for phenolic compounds. It contained phenol, o-cresol, m, p-cresol (isomer separation was not possible by GC), and at least two isomers of xylenol. It also contained several low molecular weight compounds at low concentrations. In addition, this waste water contained a small amount of suspended solids (about 50 ppm) and about 700 ppm of dissolved inorganic substances (based on a commercial analysis supplied by the company). The concentrations of the phenolic compounds were as follows:

Phenol: 579 ppm
o-Cresol: 307 ppm
m, p-Cresol: 291 ppm
Xylenols: 227 ppm

The ratio of theoretical to measured COD averaged 0.86 which indicates the presence of additional oxidizable pollutants.

We were able to obtain this waste water in limited quantities during the period when the spray column was being studied. Since the cresols and xylenols have distribution coefficients between water and isobutylene in the range from 3 to 7, they are easier to remove than phenol, which shows a distribution coefficient of 0.7 (Appendix E). Volatile solvent extraction using isobutylene was thus studied in the miniplant.

Ethylene quench waste water. The third polluted water sample was ethylene quench water produced in a naphtha-pyrolysis, olefin plant. This cracking reaction uses a complex hydrocarbo mixture as feed and is expected to produce a variety of organic side products, most of which are only slightly soluble in water (e.g., aromatic hydrocarbons, heavy tars, etc.) or are produced in small quantities (e.g., phenolics). Analysis using the GC (Porapak Q at 220°C) showed eleven major components. Five components were identified as benzene; toluene; m, p-xylene; o-xylene or ethylbenzene; and phenol. Three others correspond to light oxygenated compounds having retention times in the GC corresponding to methanol or formaldehyde, acetone, and n-propanol. Since removal of these pollutants is not practical by volatile solvent extraction in a single-solvent process, and since they are present at less than 100 ppm, a positive identification was not attempted. The remaining three components appeared to be high-molecular-weight phenolics and hydrocarbons. When the samples were received, they contained a substantial amount of floating and settled organic phases, as well as additional suspended solids which resulted in a high turbidity. The compositions of the aromatic pollutants and phenol were as follows:

Benzene:	71 to 81 ppm
Toluene:	40 to 44 ppm
Xylenes:	34 to 40 ppm
Phenol:	67 to 68 ppm

The ratio of theoretical to measured COD averaged 0.33 which indicates the importance of the unidentified pollutants.

Since phenol and the light oxygenated compounds could be recovered only by dual-solvent extraction, and since these components can be readily removed at these low concentrations by biological oxidation, this waste water was treated only by single-solvent, volatile solvent extraction using two separate solvents in different runs, isobutane and isobutylene. This treatment would be expected to remove the non-biodegradable, aromatic hydrocarbons even when operating at low values of F_s/F_w.

Oxychlorination waste water. The fourth industrial waste water is from an oxychlorination plant which produces ethylene dichloride by the following gas-phase, chemical reaction:

$$CH_2{=\!=}CH_2 + 2HCl + 1/2\ O_2 \longrightarrow CH_2Cl{-\!-}CH_2Cl + H_2O$$

The products of the reaction along with some unreacted HCl are condensed, and the aqueous phase is decanted and sent to waste. Therefore, the waste water was expected to be acidic, to be nearly saturated with ethylene dichloride, and to contain any polar side products of the reaction which would likely distribute significantly into the aqueous phase. Because these side products could include a very large number of possible chlorinated and/or oxygenated hydrocarbons containing 1 or 2 carbon atoms, the qualitative identification of pollutants was complicated. The company which supplied the waste water suggested that ethylene dichloride, chlorform, and chloral ($CCl_3{-\!-}CHO$) could be present.

Samples of oxychlorination waste water were obtained on three occasions. They showed a pronounced variation in the composition of minor pollutants; this may be the result of sample collection and storage procedures as much as actual variations due to changing conditions in the plant operation. The ranges of concentrations of HCl and organic pollutants were found to be as follows:

HCl: 1.49 to 5.78 wt. %
(determined by titration)
chloral: 14,100 to 16,900 ppm
ethylene dichloride: 1500 to 3360 ppm
ethanol: 290 to 520 ppm
acetaldehyde: 0 to 100 ppm
monochloroacetaldehyde: 0 to 300 ppm

The COD was not measured due to the high chloride concentration which interferes.

The identification of the organic compounds was based on correspondence of GC residence times (Porapak Q at 210°C) and equivalence of fraction extracted when standard and actual solutions were contacted in consecutive experiments with highly purified 2-ethyl hexanol and 1,1,2-trichloroethane. These solvents were utilized because of differences in polarity and because they boil at much higher temperatures than any of the organic pollutants and thus do not interfere with the GC analysis. Solvents used for this purpose had to be purified by repeated water washing followed by distillation so that impurities in the solvents would not interfere with pollutant analysis.

Chloral was clearly the most serious pollutant in this waste water and also the component most likely to provide a significant value from its recovery. In aqueous solution, chloral is present as chloral hydrate, $CCl_3—CH(OH)_2$, which could not be economically recovered by volatile solvent extraction. In equilibrium experiemnts it was determined that n-octanol gave a distribution coefficient for chloral in the range 15 to 50 depending on the concentration (K_d increased as chloral concentration decreased). Thus, a dual solvent process using 2-ethyl hexanol (the least expensive form of C_8 alcohol) as polar solvent and isobutane as volatile solvent was chosen for study. This waste water is presently treated in commercial operations by neutralization using any inexpensive base (e.g., limestone), followed by steam stripping. The neutralization may cause most of the chloral to react with hydroxyl ion and to form chloroform and formate ion (Pfeil, et al., 1959), in which case the chloroform but not the formate would be recovered by steam stripping.

The presence of HCl made this a very difficult waste water to handle in the miniplant because of severe corrosion. An initial attempt was made to neutralize the HCl by addition of solid NaOH so that it could be treated, but the high pH near the surface of solid NaOH led to decomposition of the chloral even though the bulk of the solution was still acidic. After trying several alternative neutralization methods, we found that by holding the waste water at 5°C while adding solid $NaHCO_3$ until the pH increased to about 5.2 (the pH of a solution of 15,000 ppm chloral in pure water), we got no appreciable chloral decomposition. However, the CO_2 which was evolved tended to sweep away most of the volatile compounds (90% of the acetaldehyde and 50% of the ethylene dichloride). This neutralization using $NaHCO_3$ was required only to protect the miniplant, and in a commercial plant the organics could be extracted from the unneutralized waste water. However, since HCl recovery is not economical in this commercial situation, the HCl would have to be neutralized after chloral extraction.

Phenol-Formaldehyde Resin Manufacture Wastewater

This wastewater was obtained form an inland plant location, where the water effluent is currently incinerated because of the absence of a plant biological oxidation system. Analysis of the water using flame-ionization chromatography with a Porapak-Q column revealed three major peaks, corresponding to methanol, formaldehyde and phenol. These three components are to be expected at high concentrations in the wastewater on the basis of the known chemistry of this process.

Quantitative analysis of the wastewater by comparison with peaks from known, standard solutions gave the following concentrations:

Component	Concentration
Methanol	12,000 ppm
Formaldehyde	17,370 ppm
Phenol	48,270 ppm

The phenol concentration in this water (4.8 wt%) was therefore the highest of any of the wastewaters studied. Clearly, simple extraction with isobutylene or isobutane would not be successful without a very high solvent/water ratio. Consequently this water was treated experimentally by the two dual-solvent processes. n-Butyl acetate was used as solvent for a test of Process II, and a mixture of 48.2% n-butyl acetate in isobutylene was used as the solvent for a test of Process III. Since numerous earlier experimental tests had shown that n-butyl acetate is readily removed from the effluent water by extraction with isobutylene or isobutane, the second extraction step with the volatile hydrocarbon solvent was not included in the testing program for this water.

Hydrofiner Condensate Wastewater

Wastewater samples were obtained from a nearby petroleum refinery, and were identified as water condensate from a hydrofining operation. This water is known to contain large quantities of ammonia and hydrogen sulfide, in addition to appreciable quantities of dissolved organics. The phenol concentration in the sample used for extraction runs was determined through peak coincidence and comparison with standard samples in flame-ionization chromatography with Porapak-Q to be 400 ppm. Quite a bit of effort was invested into searching for identification of several other smaller peaks (Herz, 1973), without significant success.

The measurement of the COD of this water was complicated by the presence of hydrogen sulfide and other sulfur-bearing compounds. A procedure was developed wherein the steps of the COD analysis were carried out as rapidly as possible, and the COD of the water was thereby found to be 17,530 ppm. It was confirmed that most of this was accounted for by hydrogen sulfide, which was not expected to be removed readily by any of the solvents under consideration. Methyl isobutyl ketone was chosen as the solvent for the extraction experiments carried out, and attention was focussed upon the removal of the 400 ppm of phenol. In industrial handling of this water, the hydrogen sulfide and ammonia would be removed by a stripping process.

Styrene Manufacture Wastewater

A sample of wastewater from a plant manufacturing styrene by the dehydrogenation of ethylbenzene was obtained through the services of the U. S. Environmental Protection Agency and Dr. John H. Coco of Gulf South Research Institute, New Orleans, La. Analysis of this water by flame-ionization gas chromatography with the Porapak Q column revealed only three significant peaks. By comparison with standard solutions of known concentration these were qualitatively and quantitatively identified as

Benzene	345 ppm
Ethylbenzene	170 ppm
Styrene	10 to 20 ppm

This sample may have come from a plant employing as a first step the process described by King (1970) and discussed in Section III wherein wastewater containing styrene is contacted with ethylbenzene (and/or benzene) so as to remove most of the styrene by extraction into the ethylbenzene (and/or benzene).

Since these compounds and any others expected to be in this wastewater are refractory to chemical oxidation as well as biological oxidation, COD measurements for this water are potentially misleading.

Because these three compounds all have high distribtuion coefficients into C_4 hydrocarbons, this water was treated by Process I, using isobutylene as the sole solvent.

Choice of Type of Miniplant Extractor

With the present state-of-the-art of solvent extraction, the development of a new process will always benefit from and will usually require testing on a pilot plant scale (Treybal, 1966). A spray column extractor was chosen for our initial experimental studies because of its inherent simplicity, its ability to handle waste waters containing suspended solids without plugging, and its flexibility of operation which makes it possible to operate at a wide range of flow rates and with either phase dispersed. In later studies, when the desirability of operation at a low solvent-to-water flow ratio had become apparent, we chose an RDC (rotating-disc contactor -- see Figure 10) to carry out experiments aimed at providing more quantitative data on mass transfer rates and backmixing. These data would be useful for scale-up and estimation of commercial feasibility. A multiple-stage mixer-settler with the means for recycling settled solvent from the settler back to the previous mixer can also be used to handle low flow ratios, but on a miniplant scale such a device would be very complex because of the need for multiple pumps and multiple agitator drives. Also, in a large-scale installation the settlers which would be required when treating waste water streams of several hundred gallons per minute become very large in horizontal cross-section (but can be short in vertical height). When many stages are required, such devices would require a large floor area, which may not be available for installing a waste water treatment

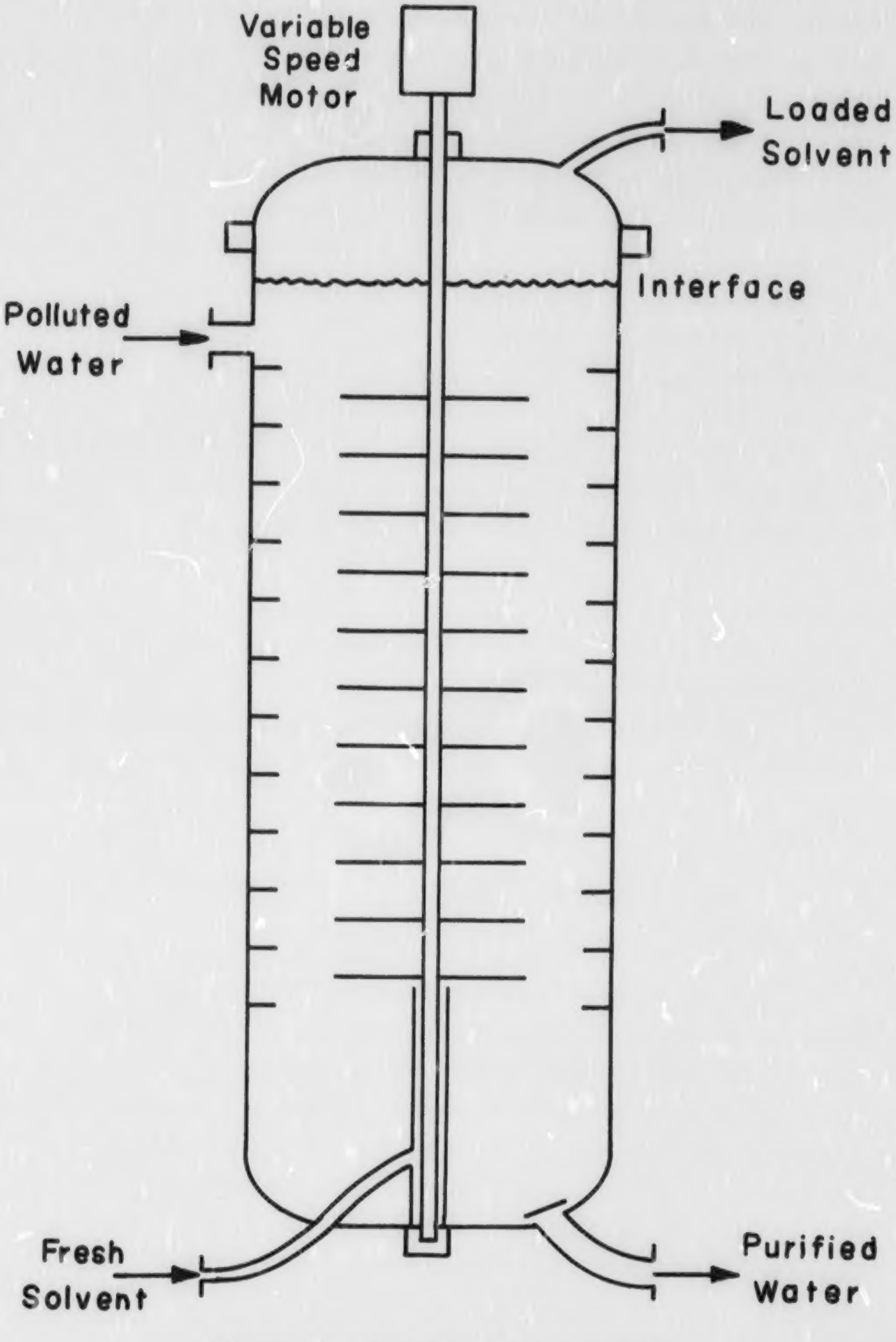


Figure 10. Rotating Disc Contactor

plant, and would require a large capital investment. One of the main advantages of mixer-settlers is their reliability of scale-up because they normally have a high stage efficiency on both scales. For this reason we felt that by gathering data only on an RDC we would be better able to develop a recommendation for choosing between these two contactors than we would had we gathered data only on a mixer-settler which would leave our understanding of the RDC short of being able to make such a recommendation.

To design any type of continuous, countercurrent extractor, a design procedure is needed which includes three main aspects (1) hydrodynamics, including droplet size estimation, flooding, and dispersed-phase hold-up, (2) axial mixing, and (3) mass transfer. Such an understanding is also needed to make the best interpretation of experimental extraction data. A general discussion which applies to the interpretation of data from both the spray column and the RDC follows.

Axial Mixing and Mass Transfer in Continuous Extractors

Solvent extraction devices can either be staged, as with mixer-settlers where the two phases are mixed and then settled within each stage, or be continuous, as with a spray column or an RDC where no separation of phases takes place except at the ends of the extractor. Axial dispersion or backmixing of one or both phases is an important design consideration in continuous extractors.

Axial mixing always tends to decrease the performance of an extractor by decreasing the mass transfer driving force below what would be predicted if the fluids passed through the device in plug flow. Mass transfer coefficients determined in small-scale equipment without consideration to axial mixing do not correspond to the coefficients similarly determined in production-scale equipment. The effects of axial mixing become more severe as the ratio of diameter to height increases, and usually become more severe with increasing diameter when this ratio remains constant. Fortunately, over the last decade considerable progress has been made in understanding and predicting the effect of axial mixing.

Axial mixing in the continuous phase is the sum of the effects of turbulent or eddy diffusion along the axis of the extractor and of channeling or radial diffusion resulting from a non-uniform velocity field (Sleicher, 1959). One experimental method for measuring axial mixing in the continuous phase involves making a steady injection of a tracer which is soluble only in the continuous phase and measuring its concentration upstream (with respect to the continuous phase) from the point of injection. This method measures only the eddy diffusion contribution to axial mixing since channeling or radial diffusion does not cause solute to move upstream. For the remainder of this report this portion of the effect of axial mixing will be referred to as "turbulent mixing." Another method for measuring continuous-phase axial mixing involves making a sudden injection of tracer and measuring the spreading of the peak by measuring the tracer concentration as a function of time at two downstream points. This method measures the contribution from a non-uniform velocity field in addition to the turbulent mixing contribution. Subsequently, the contribution to axial mixing due to a non-uniform velocity field will be referred to as "channeling." In using this term we do not mean to imply the type of channeling that can occur in a small diameter packed bed where most of the liquid flows close to the wall, but rather we refer to the type of non-uniform flow like that which occurs in an open pipe in the laminar flow regime. The sum of the effects of turbulent mixing and channeling is the significant measure of axial mixing when solute is being transferred from one phase to the other in a solvent extraction column. Other experimental methods for measuring axial mixing are discussed in a review by Ingham (1971).

Axial mixing in the dispersed phase is somewhat more complex than for the continuous phase, and it includes the effects of turbulent mixing, of mixing caused by the distribution of droplet sizes and thus a distribution of residence times (often called forward mixing), and of coalescence and redispersion of the droplets (Ingham, 1971). The various models which have been proposed to account for axial mixing in extraction columns have recently been reviewed (Misek and Rod, 1971) and include the stage model (Young, 1957), the backflow model (Sleicher, 1960; Miyauchi and Vermeulen, 1963), the dispersion model (Sleicher, 1960; Miyauchi and Vermeulen, 1963), and a combined model which includes forward mixing effects (Olney, 1964). A random walk model has been used in single-phase flow in packed-beds (Jacques and Vermeulen, 1957; Cairns and Prausnitz, 1960).

The stage model uses only one parameter to represent the mixing in both phases and is usually inadequate (Misek and Rod, 1971). The backflow and dispersion models have been shown to be equivalent in the limit as the effective number of stages for backflow becomes large (Hartland and Mecklenburgh, 1966); both models require two parameters to represent the backmixing, but the stage model also defines a number of stages. The combined model is much more complex as it requires a knowledge of the dispersed phase droplet size distribution. For the purpose of evaluating the data taken in this report, we have chosen to use the dispersion model. The details of the dispersion model are developed in Appendix C.

If the counterflowing fluid phases are assumed to move in plug flow with no axial mixing, then the relationship between the terminal concentrations can be expressed as follows (Colburn, 1939):

$$\eta = \frac{X_{wo} - X_{si}/K_d}{X_{wi} - X_{si}/K_d} = \frac{E - 1}{E \cdot \exp\,[(1 - 1/E)\,N_{ow}] - 1} \qquad (1)$$

where

η = Dimensionless concentration change defined by the first equality,

X_{wo} = Pollutant concentration in the outlet water phase,

X_{wi} = Pollutant concentration in the inlet water phase,

X_{si} = Pollutant concentration in the inlet solvent phase,

E = Extraction Factor = $K_d \cdot F_s/F_w$,

N_{ow} = Number of overall water-phase transfer units.

It is assumed in the derivation of this equation that K_d, F_s, F_w and the overall water-phase mass transfer coefficient per unit volume of extractor, $K_{ow}a$, are constant throughout the extractor. If the solutions are dilute, these assumptions will hold when the concentrations are measured in weight fractions and the flow rates are measured in weight per unit time. However, when F_s/F_w is small and extraction is efficiently carried out, then the concentrations in the solvent phase can be large even though X_{wi} is small. In this case it is usually better to measure concentrations in weight ratios (lb. pollutant/lb. pollutant-free fluid) and to measure flows as weight pollutant-free fluid per unit time. As long as the two fluids are mutually immiscible, flows measured in this manner will be constant.

Equation (1) can be expressed simply as follows:

$$\eta = f(E,N_{ow}) \qquad (2)$$

Similarly, for the case where axial mixing is predicted by the dispersion model, an expression is developed in Appendix C which is of the following form:

$$\eta = f(E, N_{ow}, Pe_w, Pe_s) \qquad (3)$$

where

Pe_w = Water-phase Peclet number,

Pe_s = Solvent-phase Peclet number.

These two dimensionless parameters characterize the extent of axial mixing in each phase. When $Pe_w = Pe_s = \infty$, equation (3) is the same as that for plug flow. When Pe = 0 for one or both phases, equation (3) expresses the overall concentration change when that phase is completely mixed (i.e., has a concentration equal to its outlet concentration at all points in the extractor). The effect of axial mixing is illustrated in Figure 11 where the case for Pe_w = 10 and Pe_s = 20 is compared to that for plug flow. For a given number of transfer units, the decrease in removal efficiency due to axial mixing is most significant when E is greater than 1.

Equation (3) may be used in the evaluation of experimental data as well as in the design of large-scale extractors. For many types of extractors, correlations are available in the literature which relate Pe_w and Pe_s to the flow velocities, droplet sizes, extractor dimensions, and physical properties of the two phases. If the overall extraction efficiency is measured experimentally and used to calculate η, then with Pe_w and Pe_s

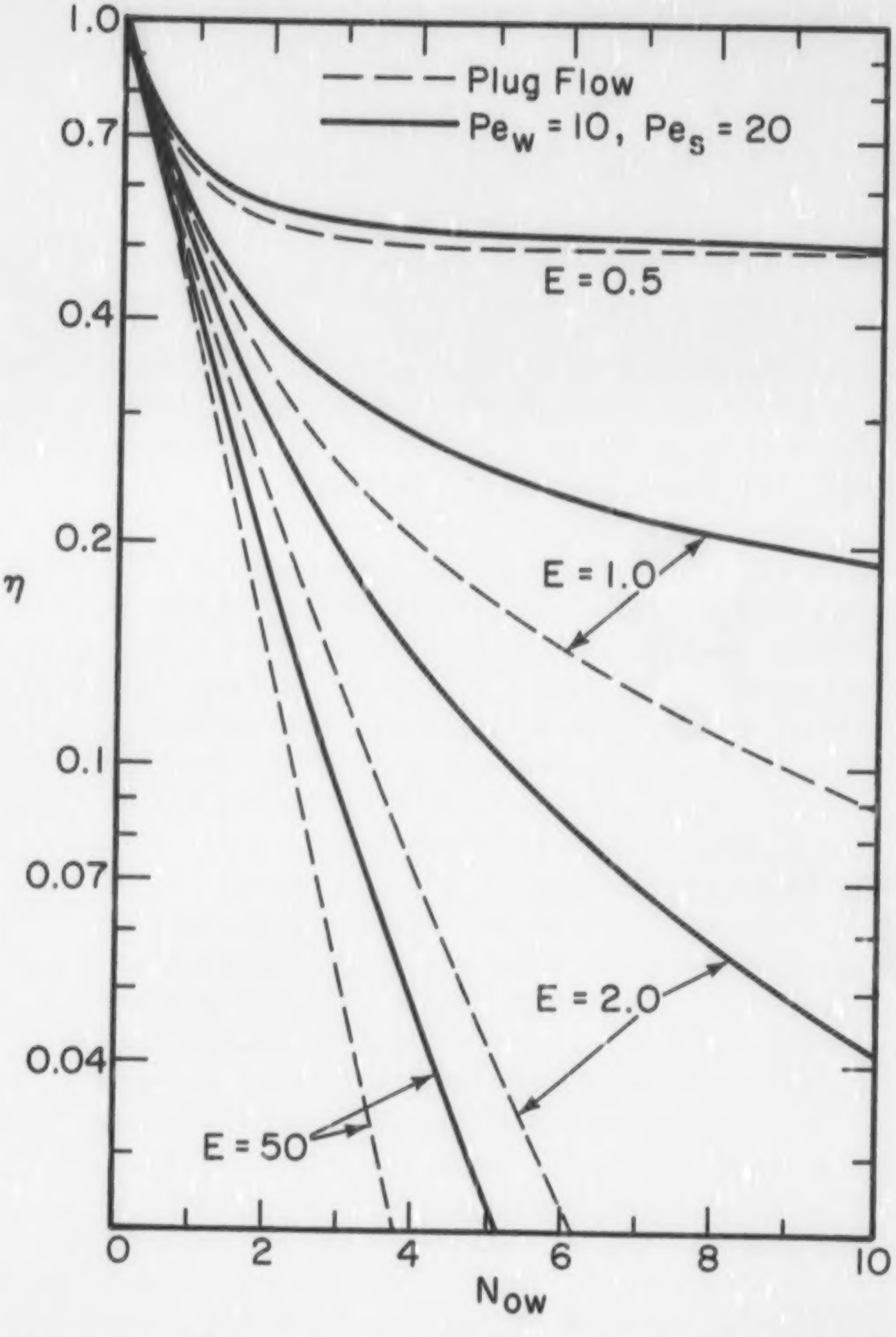


Figure 11. Comparison of Plug Flow and Dispersion Models

determined from correlations and E determined from the measured flow rates and the separately measured distribution coefficient, equation (3) may be solved implicitly to give a value of N_{ow} for each solute in the feed water.

The usual method of correlating mass transfer data obtained from an experiment is to correlate the individual mass transfer coefficients in the separate phases. Thus, if a correlation is developed for the mass transfer coefficient in the water phase and another for that in the solvent phase, then by assuming that the resistances are additive, the overall mass transfer coefficient may be calculated at conditions different from the actual experiment. The validity and limitations in the additivity assumption have been described by King (1964). Since the number of transfer units is simply related to the mass transfer coefficient per unit volume (k·a where a is the interfacial area per unit volume), the additivity of resistances can be expressed as follows:

$$\frac{1}{N_{ow}} = \frac{1}{N_w} + \frac{(1/E)}{N_s} \qquad (4)$$

where

N_w = Number of water-phase transfer units,
N_s = Number of solvent-phase transfer units.

There are a number of expressions available which relate N_w and N_s to physical size and flow parameters and to solute diffusivities in the two phases; several such expressions are discussed in Appendix B and are used for purposes of comparison with data taken in this project. In a single experiment where several solutes are simultaneously extracted, the physical size and flow parameters are the same for each solute. In many cases the solute-to-solute variation in diffusivity in the water phase (and in the solvent phase) is small, so the solute-to-solute variation in N_w (and N_s) is also small. The influence of the resistance to mass transfer in one phase on the resistance in the other phase can also lead to minor variations in N_w and N_s from solute to solute. However, according to equation (4) a plot of $1/n_{ow}$ vs $1/E$ should result approximately in a straight line since solute-to-solute variations in N_w and N_s are much less than solute-to-solute variations in E.

As illustrated by equation (3) and in Figure 11, once Pe_w and Pe_s are specified the dispersion model allows η to be calculated for each pair of values of E and N_{ow}. From the set of values of E and N_{ow} which give a specified value of η, a plot of $1/N_{ow}$ vs $1/E$ may be prepared. Such a plot is illustrated in Figure 12 for $Pe_w = 10.0$ and $Pe_s = 20.0$ where η, defined in equation (1), is the parameter (actually Figure 12 is a cross plot from Figure 11). Superimposed on Figure 12 is a straight line, as suggested by equation (4), for a case where $N_w = 5.0$ and $N_s = 8.0$ (typical of operation in the miniplant RDC at a low flow ratio). Thus for any value of E, the corresponding value of N_{ow} may be determined from the straight line using the ordinate, and the corresponding value of η may be determined by interpolation between

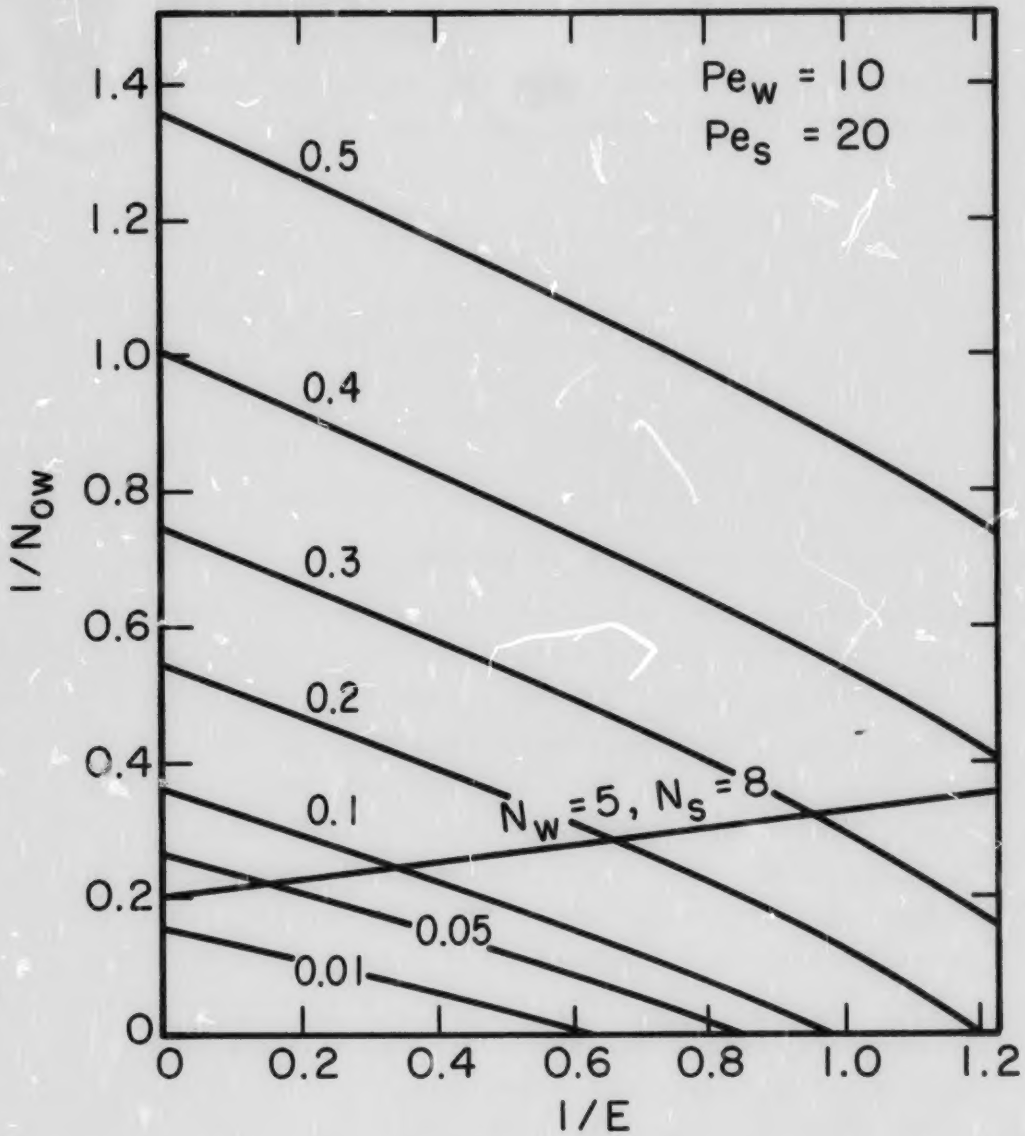


Figure 12. Plot of Equation 3 to Illustrate Additivity of Resistances. Parameter is η.

lines of constant η.

The values of N_w and N_s which result from the above type of analysis of experimental data may be used to calculate the individual-phase mass transfer coefficients from the following equations once a is determined as described below:

$$k_w = \frac{N_w \, (F_w/A)}{a \, H} \qquad (5)$$

$$k_s = \frac{N_s \, (F_s/A)}{a \, H} \qquad (6)$$

where A = Cross-sectional area of column,

H = Total height of column.

By comparing the values of the individual-phase mass transfer coefficients with those predicted from various models in the literature, the experimental data can be used to infer the answers to such questions as, "Do the dispersed-phase droplets act as rigid spheres, or do they show internal circulation?" and "Is interfacial turbulence important, or do surface-active impurities inhibit mass transfer?" The lack of a priori answers to these types of questions is what makes pilot-scale experimentation a necessary part of developing a new solvent extraction process.

In this report the dispersion model has been used to solve two distinct types of problems which involve the analysis of continuous extraction devices. In the Type 1 problem, the overall column height and the two phase velocities are specified. If the removal efficiency is to be estimated, then the physical properties for each phase are used with three correlations for predicting (1) the hydrodynamics of the phases (from which the hold-up and interfacial area per unit volume are calculated), (2) the axial dispersivities, ε_w and ε_s (from which Pe_w and Pe_s are calculated - see Appendix C), and (3) the individual-phase mass transfer coefficients, k_w and k_s (from which N_{ow} is calculated using equations 4, 5, and 6). Equation (3) can then be used directly to calculate $\hat{\eta}$ and the removal efficiency. If the removal efficiency has been measured and N_{ow} is to be calculated, then the physical properties and the same correlations are used to estimate the hydrodynamics and Pe_w and Pe_s. In this case equation (3) must be solved implicitly for N_{ow}.

In the Type 2 problem, the overall column height is not specified, but rather it must be calculated to provide a specified removal efficiency. Since the column height enters into N_{ow}, Pe_w, and Pe_s, equation (3) is more difficult to use. In this project a method has been used in which H is assumed and the removal efficiency is calculated as for a Type 1 problem. The correct value for H is then determined by trial-and-error calculation. Pratt (1975) has recently proposed a more direct calculation which avoids this trial-and-error procedure. The correlations which were used for hydrodynamics, axial mixing, and mass transfer for both the spray column and the rotating disk contactor for both types of problems are discussed in detail in Appendix B, to which the reader is referred at this point.

SECTION VI

EXPERIMENTAL APPARATUS AND PROCEDURES

To carry out the experimental program described in Section V, apparatus and procedures had to be developed for (1) the analysis of aqueous- and organic-phase samples taken during the treatment of both actual and simulated waste waters, (2) the measurement of equilibrium distribution coefficients for various solute-solvent combinations, (3) the continuous, countercurrent contacting of actual and simulated waste waters with both volatile solvents and less-volatile, polar solvents, (4) the continuous regeneration of volatile solvents by distillation in equipment designed for operation at moderate pressures (up to 50 psig), and (5) the batch-wise regereration by atmospheric distillation of less-volatile, polar solvents. During the project the equipment and techniques were continually modified and improved as problems were encountered and solved. In the discussion to follow, the final arrangement will be described along with the most important modifications made during the project.

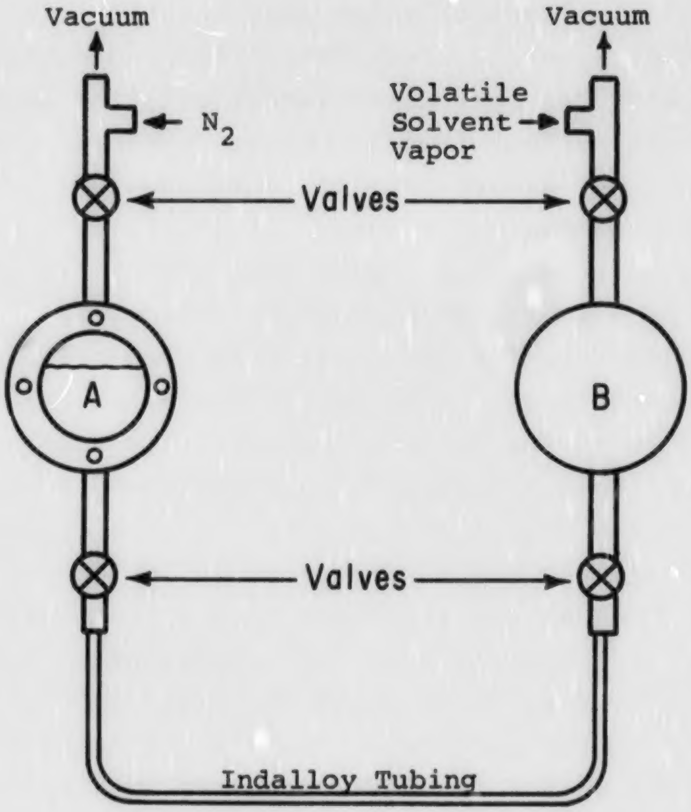
Analytical methods. The quantitative analyses of aqueous-phase samples and samples of polar solvent solutions during extraction mini-plant runs were made by injection of 0.3 to 6μl samples into a Varian (Model 600-D) gas chromatograph equipped with a Varian (Model 328) temperature controller and a flame ionization detector. For aqueous-phase samples, 0.8μl injections made using a Hamilton (Model 7001) microliter syringe were found to be reproducible giving a precision of ± 2 - 4% depending on the concentration and type of organic solute present. Larger volume injections using a Hamilton (Model 701) ten microliter syringe were occasionally used for very dilute samples, but reproducibility fell to ±5 - 8% when using this larger syringe. Injections greater than 8μl usually extinguished the flame. For polar solvent solution samples, 0.5μl injections were always used as larger volumes tended to saturate either the column or the detector giving an erratic peak size for the polar solvent. Separate syringes for aqueous- and organic-phase injections were used to minimize the difficulty in flushing residue from the syringes.

The flow of helium carrier gas was maintained at 20 - 30 ml/min through a 3 foot length of 1/8-inch, stainless steel, packed chromatographic column. The packing material found most universally useful was Porapak Q (100 - 120 mesh) operated at temperatures between 170 and 240°C. The temperature was chosen to allow the separation of peaks while giving a minimum time for the peak of longest retention time to be completely emitted. In one case when a water sample containing benzene and n-butanol was analyzed, a 3 foot length of column containing Porapak T (80 - 100 mesh) at 180°C was used to provide an adequate separation of peaks when it was found that they could not be separated using Porapak Q.

One problem often encountered after a column had been used for several weeks was the appearance of unexplained peaks. Such peaks, which would appear even when pure distilled water was injected, may result from an accumulation of organic material on the first few inches of column that either reacts with or is stripped by the water sample. The retention time was reproducible, but the peak size for these anomolous peaks usually varied by about ±20%. As long as the unexplained peak did not overlap with a peak from an important constituent in the sample this problem could be tolerated. If necessary, the unexplained peaks could be eliminated by preparing, installing, and conditioning a new column. During all analyses, occasional pure water injections were made to check for such anomolous peaks.

The hydrogen flow to the flame ionization detector was maintained at 20 - 30 ml/min; the air flow at about 300 ml/min. A small flow controller and a cartridge filter were installed on both the helium and hydrogen flow lines. The combination of a Porapak column and a flame ionization detector worked particularly well for aqueous samples since the water retention time was short (10 to 15 sec.) and the water response was very small. Therefore, the water peak passed quickly through the column and did not interfere appreciably with the other peaks. In addition to the analyses using gas chromatography, the chemical oxygen demands (COD) of the feed waste water and of the purified product water were determined for the experiments in which industrial waste water was treated. The ASTM standard procedure (ASTM, 1970) was employed which uses potassium dichromate in 50% sulfuric acid with silver sulfate as catalyst to oxidize all organic substances in the sample. To reduce the loss of volatile organics, the sample was cooled in an ice water bath while the sulfuric acid was being added to the sample (EPA, 1971). The determination of COD was useful when the waste water contained substances of very low volatility which were not detected by gas chromatography.

The quantitative analyses of samples of volatile solvent were made using a technique developed by Fleck and Prausnitz (1968) and improved in this work. During an extraction experiment each sample was collected in a 60 ml sample holder, as described below under "Experimental Procedure". Following the experiment, the sample holder was pressurized to a total pressure of about 50 psig with dry nitrogen, was connected to another 60 ml container by an 8 inch length of soft, Indalloy (Indalloy #5 with a melting point of 134°C, Indium Corporation of America) tubing (1/16" o.d. with a 0.010" hole) as shown in Figure 13, and the empty container and tubing were evacuated. Gaseous volatile solvent was then added to the empty container and tubing until the pressure was slightly below the room temperature vapor pressure of the volatile solvent. The valves on both ends of the Indalloy tubing were opened and about 20 ml of volatile solvent solution was allowed to flow through the tubing. With the liquid still flowing, the tubing was pinched off and cut at the center



A - 60-ml Sample Holder with Glass Front

B - 60-ml Brass Container

Figure 13. Volatile Solvent Sampler

with a Varian swaging tool, and then the Indalloy tubing was swaged into about 10 pieces each 3/4 to 1 inch in length. These encapsulated samples of volatile solvent solution were dropped into a beaker of water to check for leaking volatile solvent and then were taken immediately for analysis.

A Perkin-Elmer (Model 990) gas chromatograph equipped with dual columns and a temperature programmer was used for quantitative analysis of volatile solvent solutions and for all analyses associated with the determination of equilibrium distribution coefficients. An induction heater was attached to the injection port of the chromatograph allowing the Indalloy-encapsulated samples to be melted in a stream of carrier gas flowing directly into one of the columns. As the low-melting, Indalloy melted, the entire sample of volatile solvent solution was vaporized into the chromatograph. The temperature of the chromatograph was initially held at 150°C until the volatile solvent peak was detected, then the temperature was increased to a level allowing the solute peaks to be quantified. The same type of packing and the same gas flow rates were used with both chromatographs.

The response factors of both chromatographs were found to vary significantly with such variables as gas flow rates and column temperature. Such day-to-day variation made frequent calibrations an essential part of the analytical procedure. For the analysis of aqueous and polar solvent solutions, a standard solution of approximately the same composition as the unknown was prepared by weight, using an analytical balance which reads to ± 0.1 mg. Three repetitive injections were made with both the standard and the unknown solutions, and the composition of the unknown was determined from the average responses assuming that peak area was proportional to concentration over the slight concentration differences between unknown and standard. Peak areas were determined by a disc integrator except when peak overlap occurred, in which case a procedure of cutting out and weighing peaks was found to be considerably more accurate. Typically the concentrations determined in this manner are accurate to ± 2 - 4%.

The calibration procedure for volatile solvent solutions was more difficult since the total quantity of sample was not precisely controlled with the encapsulated samples. A gas-tight, 0.5 cc (Precision Sampling) syringe was used to inject very accurate and precise volumes of pure volatile solvent vapor into the gas chromatograph. By measuring the pressure and temperature of the gas in the syringe, the mass injected was determined and a response factor curve was prepared. The response factors for the solutes were determined separately by injection of standard solutions of these solutes in methanol using the microliter syringe.

With the response factors thus determined for each component in the volatile solvent sample, its composition could be calculated. Comparison with prepared standard solutions of solutes in volatile solvent indicated that the accuracy of volatile solvent analyses was ±5%.

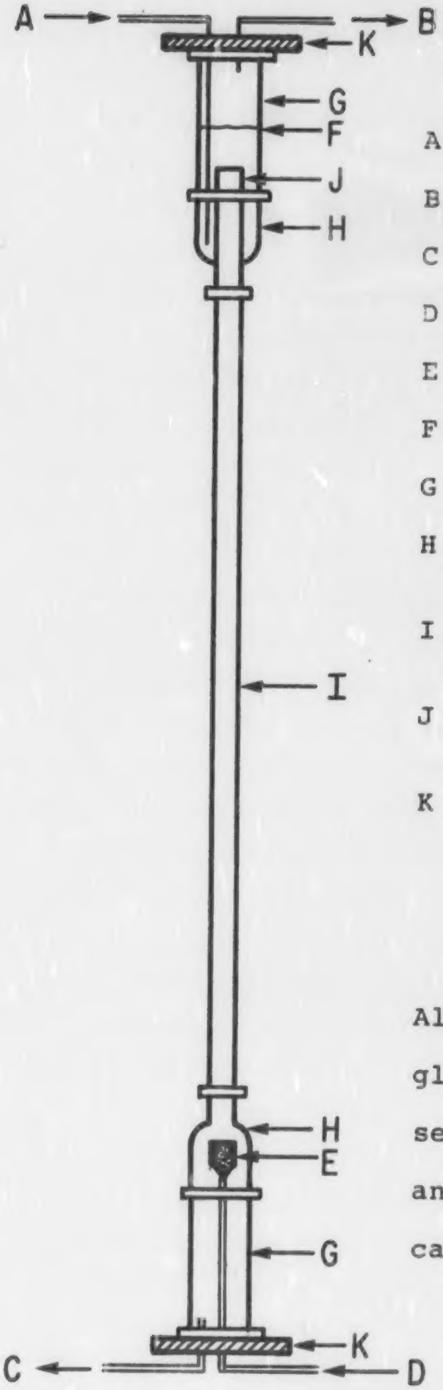
The samples of both aqueous- and organic-phase solutions were usually analyzed within two days of when they were collected. During this period the samples were stored at 4°C to minimize biological oxidation. During the period in which experiments with the spray column were conducted, the non-volatile samples were stored in 5 cc vials with a plastic cap and a paper seal. Later it was determined that some organic solutes in aqueous samples were absorbed into the paper seals, causing a decrease in concentration of as much as 1.5% per day for a 300 ppm solution of n-butyl acetate. For all subsequent experiments the paper seals were replaced by a Teflon disc which completely eliminated this problem.

Equilibrium Determinations. Controlled measurements of equilibrium distribution coefficients were made for a large number of solute-solvent systems pertinent to this work. The apparatus and procedure used and the results obtained for these systems are reported in Appendices E and F.

Spray column extractor. For the initial experimental studies, a small spray column extractor was constructed following the design suggestions of Blanding and Elgin (1942). The distance between the distributor plate and the main interface was 42 inches, and the column diameter was 1 inch. The design capacity at 25% of flooding was for a water flow rate of 1.0 gal/hr and for a C_4 hydrocarbon flow rate of 3.4 gal/hr.

As shown in Figure 14, the column was built using 5 pieces of industrial glass pipe with appropriate flanges and gaskets. The use of the glass contactor made it possible to observe the motion of the fluid phases, and thereby to judge the accuracy of design drop size calculations, the degree of turbulence, the possible flotation of solid particles, and other performance characteristics. All flow line and temperature well connections were through two brass end plates to eliminate the need for glass blowing with its expected reduction in the strength of the tempered glass pipe. As purchased, the maximum safe operating pressure for the glass pipe was 50 psig, which is only about 8 psi above the expected operating pressure when using isobutane as solvent.

The design of the distributor plate has a very important effect on the performance of a spray column. For operation with the hydrocarbon phase dispersed, the drops were formed by forcing the solvent to flow up through 30 holes of 1/16 inch diameter (Figure 15A). The holes were formed by drilling through a 1 inch diameter circular disc of stainless steel without removing the burrs formed by the exit of the drill. The flow line connections were designed so that the column could be inverted to study operation with the aqueous phase dispersed. To obtain uniform drops of water, a different distributor plate was required. Satisfactory operation was achieved when water was forced to flow down through 7 holes of 1/16 inch diameter drilled through a Teflon disc of 1 inch diameter (Figure 15B). Holes drilled



A - Continuous Phase Inlet

B - Dispersed Phase Outlet

C - Continuous Phase Outlet

D - Dispersed Phase Inlet

E - Distributor Plate

F - Main Interface Position

G - 2"-diameterX6" Glass Pipe

H - 2" to 1" Glass Pipe Reducer

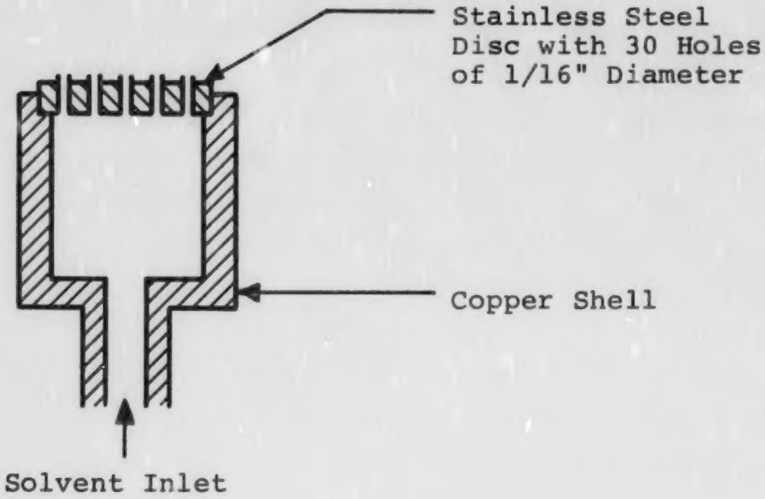
I - 1"-diameterX36" Glass Pipe

J - 1"-diameter Glass Tubing (attached by epoxy resin)

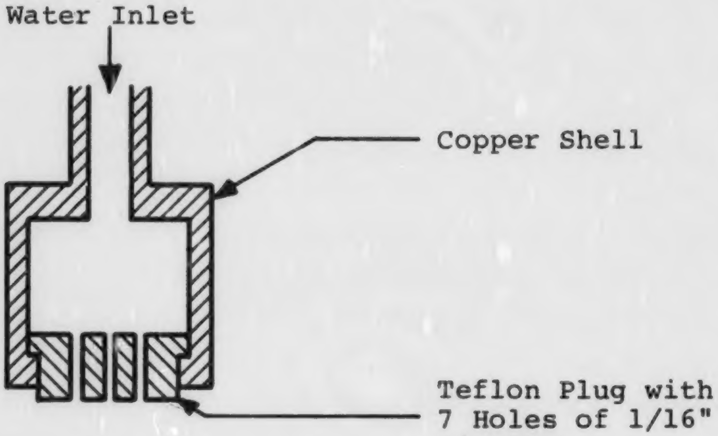
K - Brass End Plate

All glass-to-glass and glass-to-brass joints separated by Teflon gaskets and attached by standard cast iron flanges.

Figure 14. Spray Column Extractor



A. Solvent Distributor Plate

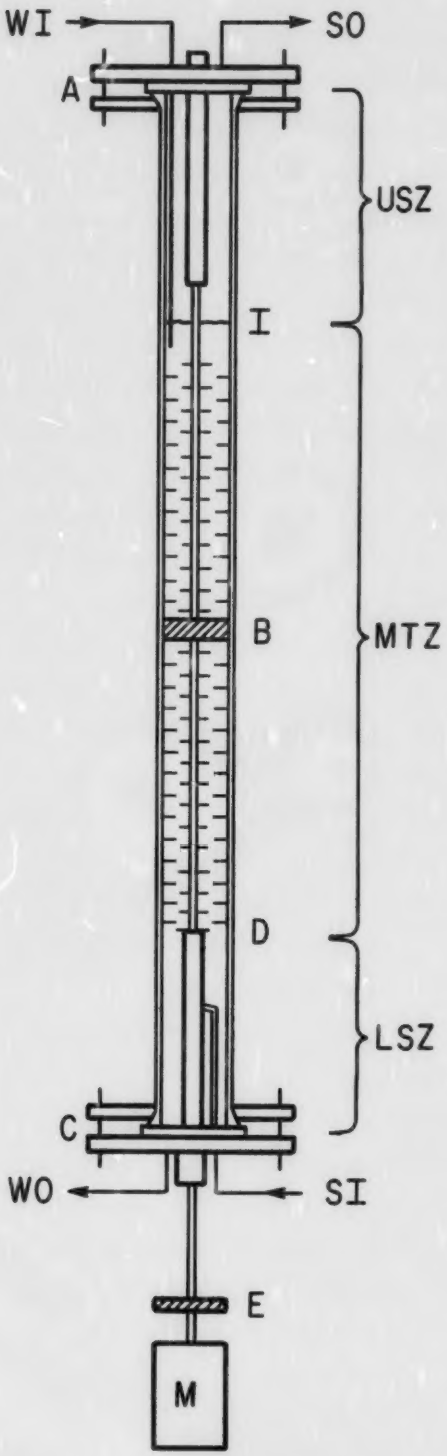


B. Water Distributor Plate

Figure 15. Distributor Plates

through copper did not result in aqueous drops of a uniform size.

Rotating disc contactor. After initial experiments, the spray column extractor was replaced with an RDC to obtain effective operation and representative mass transfer data while operating with a low flow ratio. As shown in Figure 16, the outer shell of the RDC was a 4 foot length of 3 inch diameter industrial glass pipe, and the internal shaft, discs, stators, and support rods as well as the external end plates were built from type 316 stainless steel. The total 48 inch length was divided into a 29 inch length of active mass transfer region and two quiescent zones of about 10 inches at either end for disengagement of the phases. A stationary tubular shield surrounding the rotating shaft extended 9 inches from each end plate to reduce turbulence in these quiescent zones. The design capacity was for a water flow rate of 5.0 gal/hr when the mass ratio of solvent-to-water flow was 0.3 or less. Not shown on Figure 16 but present on the pilot plant RDC, a 4 foot length of 6 mm glass tubing was connected by stainless steel tubing through the end plates to serve as a sight glass. The vertical distance between the level of the interface within the sight glass and that in the column divided by the vertical distance between the interface in the column and the bottom rotating disc provided an estimate of the solvent hold-up in the mass transfer zone of the column.



A - Upper End Plate

B - Mid-column Bearing

C - Lower End Plate

D - Dispersing Disc

E - Ball Bearing

I - Main Interface

M - Variable Speed Electric Motor

WI - Polluted Water Inlet

WO - Purified Water Outlet

SI - Fresh Solvent Inlet

SO - Loaded Solvent Outlet

USZ - Upper Settling Zone

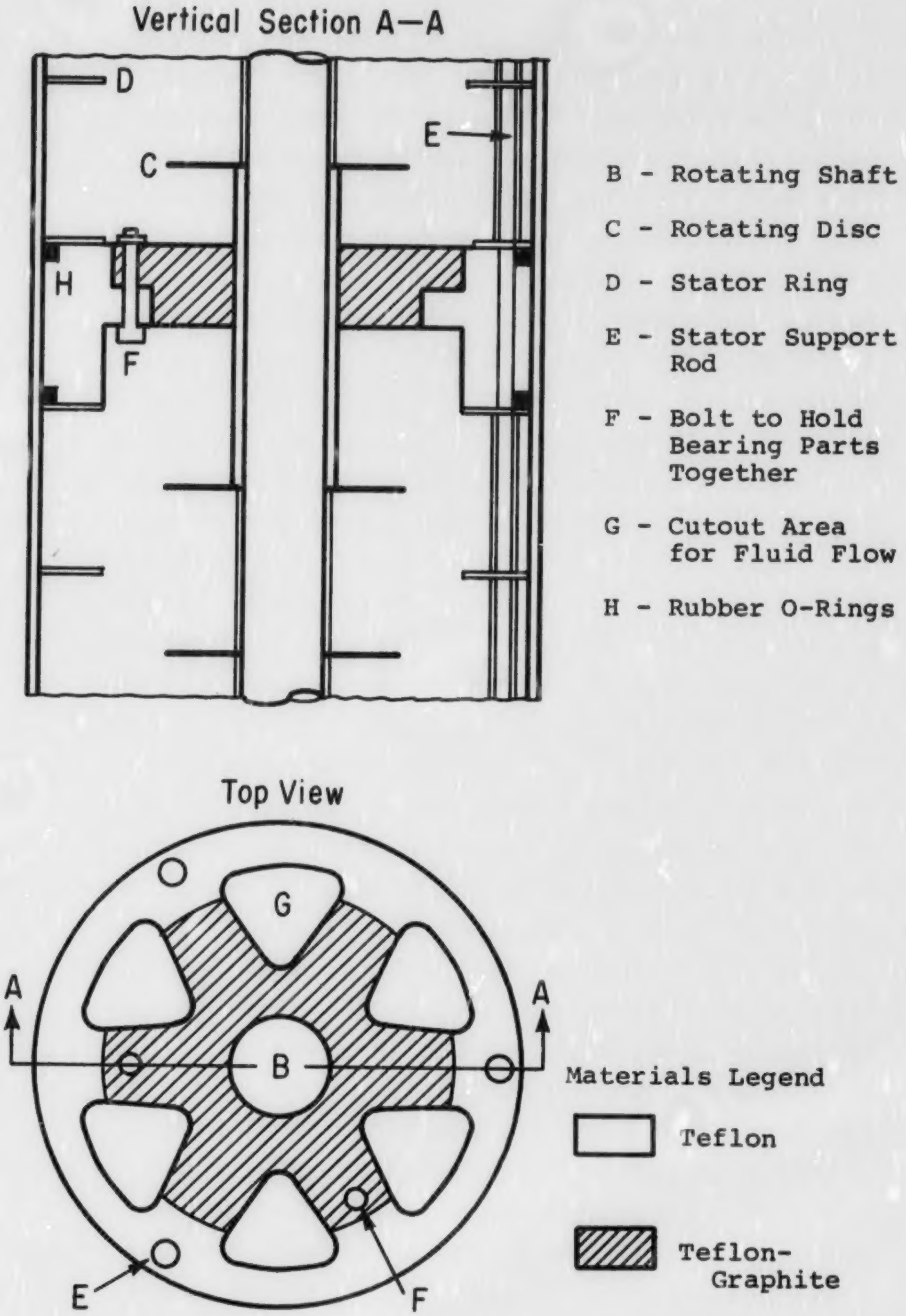
MTZ - Mass Transfer Zone

LSZ - Lower Settling Zone

Figure 16. Rotating Disc Contactor

The rotating discs were 0.035 inch thick with a 1/2 inch hole so that they would just slide along the 1/2 inch rotating shaft. Discs of 1.50 and 1.75 inch diameter could be interchangeably attached to the shaft. The discs were held firmly in position by a threaded tightening nut at one end, a fixed sleeve at the other end, and 1 inch lengths of tubing (0.506 inch i.d.; 0.563 inch o.d.) which acted as spacers to separate each pair of discs. The stators were 0.035 inch thick with an outside diameter slightly less than the 3 inch inside diameter of the glass pipe. Interchangeable stators with holes of 2.00 and 2.25 inch diameter were used. The stators were held in position by 3 rods of 3/16 diameter running the entire length of the column. Spacers of 1 inch length were used to separate the stators, and threaded tightening nuts were used at each end of the rods.

To minimize vibration of the rotating shaft, it was necessary to install a bearing midway through the column. As with the stators, this bearing was held in position by the three 3/16 inch rods plus two rubber o-rings which pressed firmly against the glass pipe when the tightening nuts on the rods were tightened. The details of this bearing, built of Teflon with a 35% graphite - 65% Teflon solid inner bearing surface, are shown in Figure 17. The cut-out area, which allowed the fluids to flow past the bearing, provided an open area about 24% of the total column cross-sectional area. There were 12 discs above the bearing and 14 discs below it.



B - Rotating Shaft

C - Rotating Disc

D - Stator Ring

E - Stator Support Rod

F - Bolt to Hold Bearing Parts Together

G - Cutout Area for Fluid Flow

H - Rubber O-Rings

Materials Legend

☐ Teflon

▨ Teflon-Graphite

Figure 17. Mid-Column Bearing

The rotating shaft of the RDC was driven by a 1/4 hp electric motor with a continuously variable speed control (Minarik Model SL61) capable of providing rotational speeds between 400 and 1600 RPM. The rotational speed was calibrated with a stroboscope and was reproducible to ±5 RPM. The motor was located about 12 inches below the bottom end plate, and a ball bearing supported the shaft just above the flexible coupling which connected the motor shaft to the shaft of the RDC. As shown in Figure 18, a rotating seal (U.S. Seal Model PS-903) provided a positive seal where the shaft passed through the bottom end plate. Just above the seal, a Teflon-graphite insert provided a bearing surface for the rotating shaft; a similar bearing was installed in the upper end plate, but no seal was required on the upper end.

The RDC was always operated with the solvent phase dispersed. The solvent entered through a length of 1/4 inch tubing which carried it into the area between the rotating shaft and the stationary tubing which surrounded the shaft. A short length of Teflon tube was attached to the top of the stationary stainless steel tubing; this Teflon tube extended upward to within 1/16 inch of the bottom rotating disc. Since the solvent preferentially wetted the Teflon, a thin film of solvent was emitted so that the shearing action of the bottom disc broke it into small droplets.

When the column was in operation, the main solvent-water interface was positioned about 2 inches above the top disc (Figure 19). The inlet water

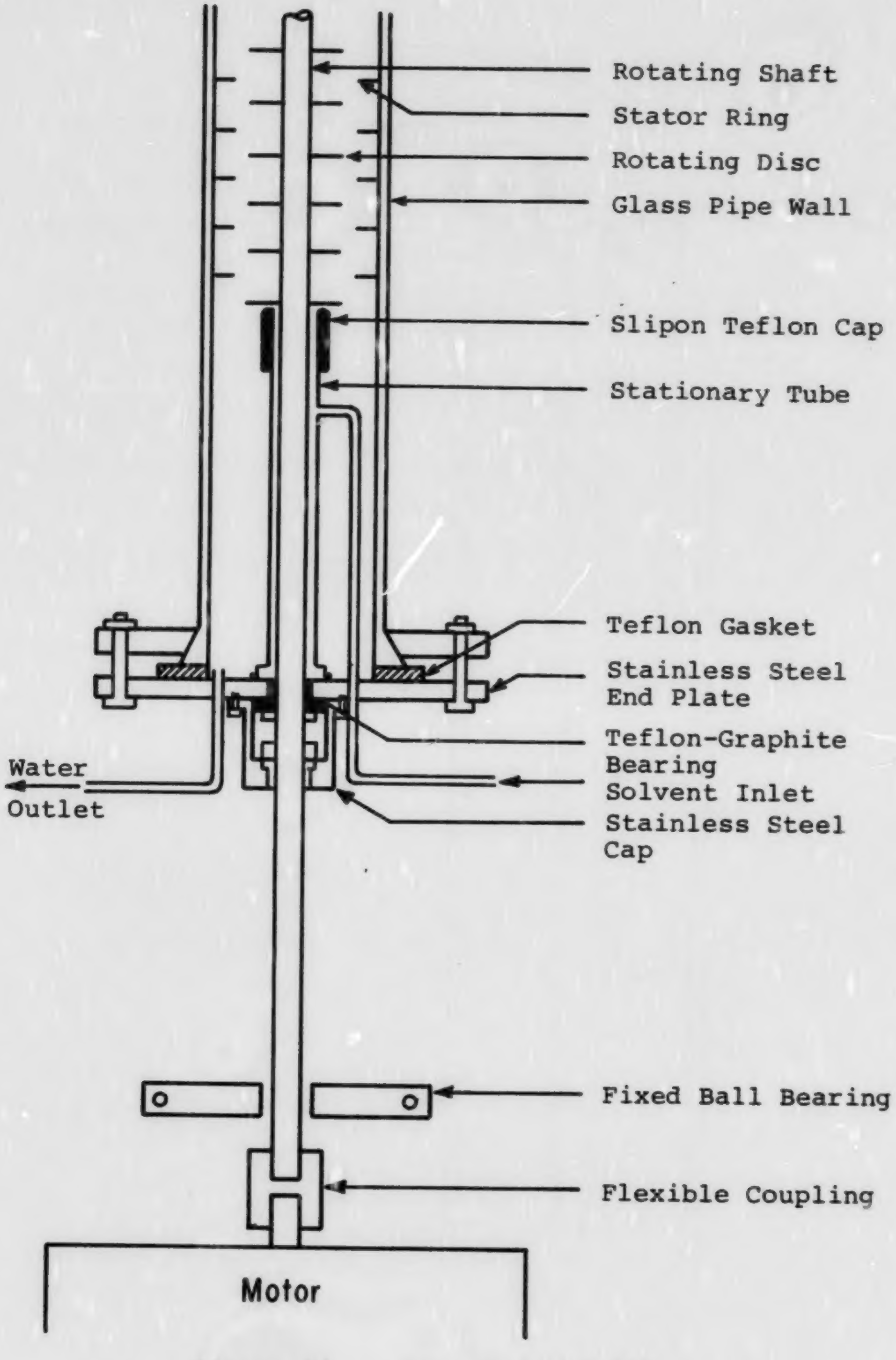


Figure 18. Lower Part of RDC

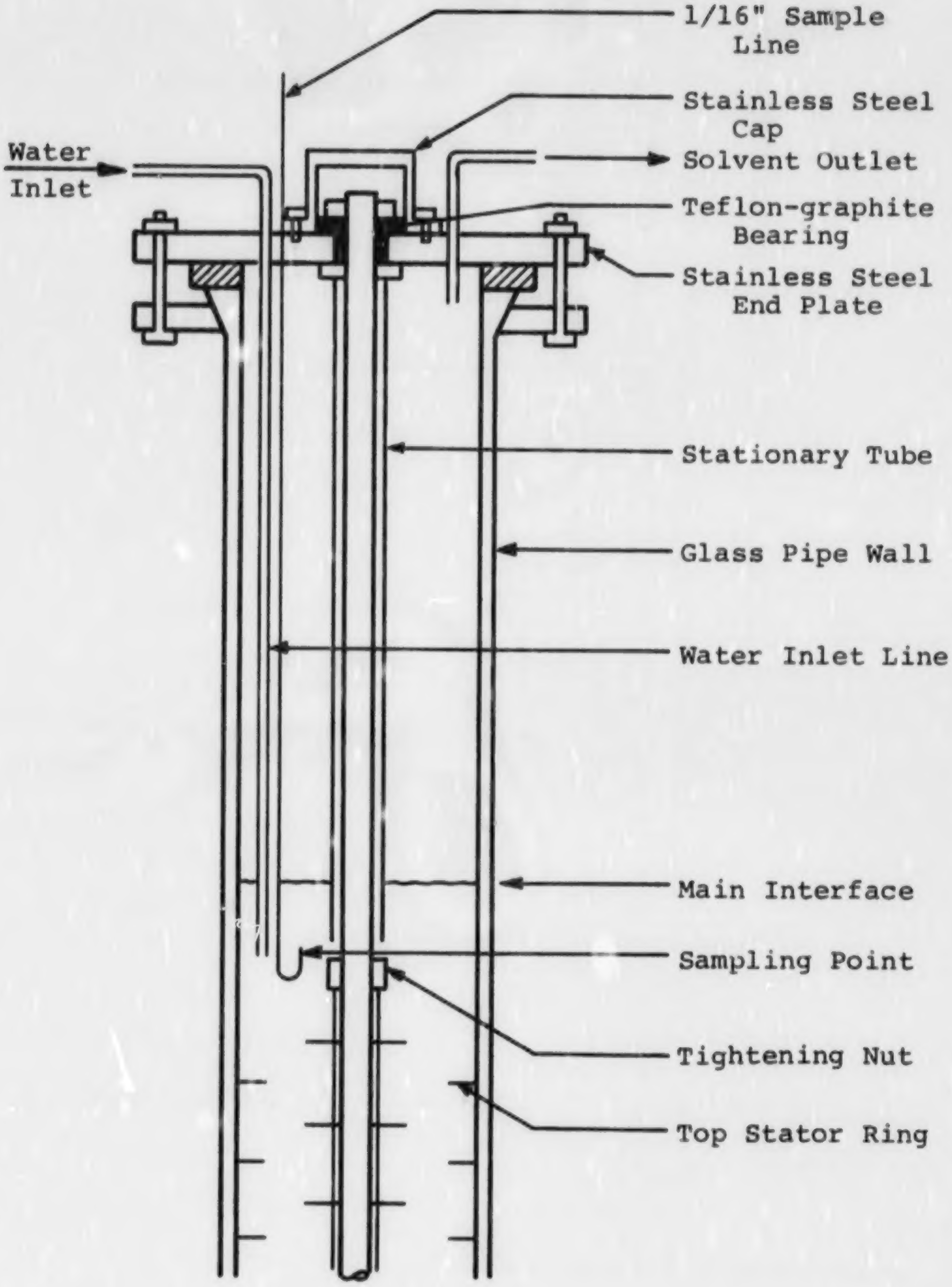


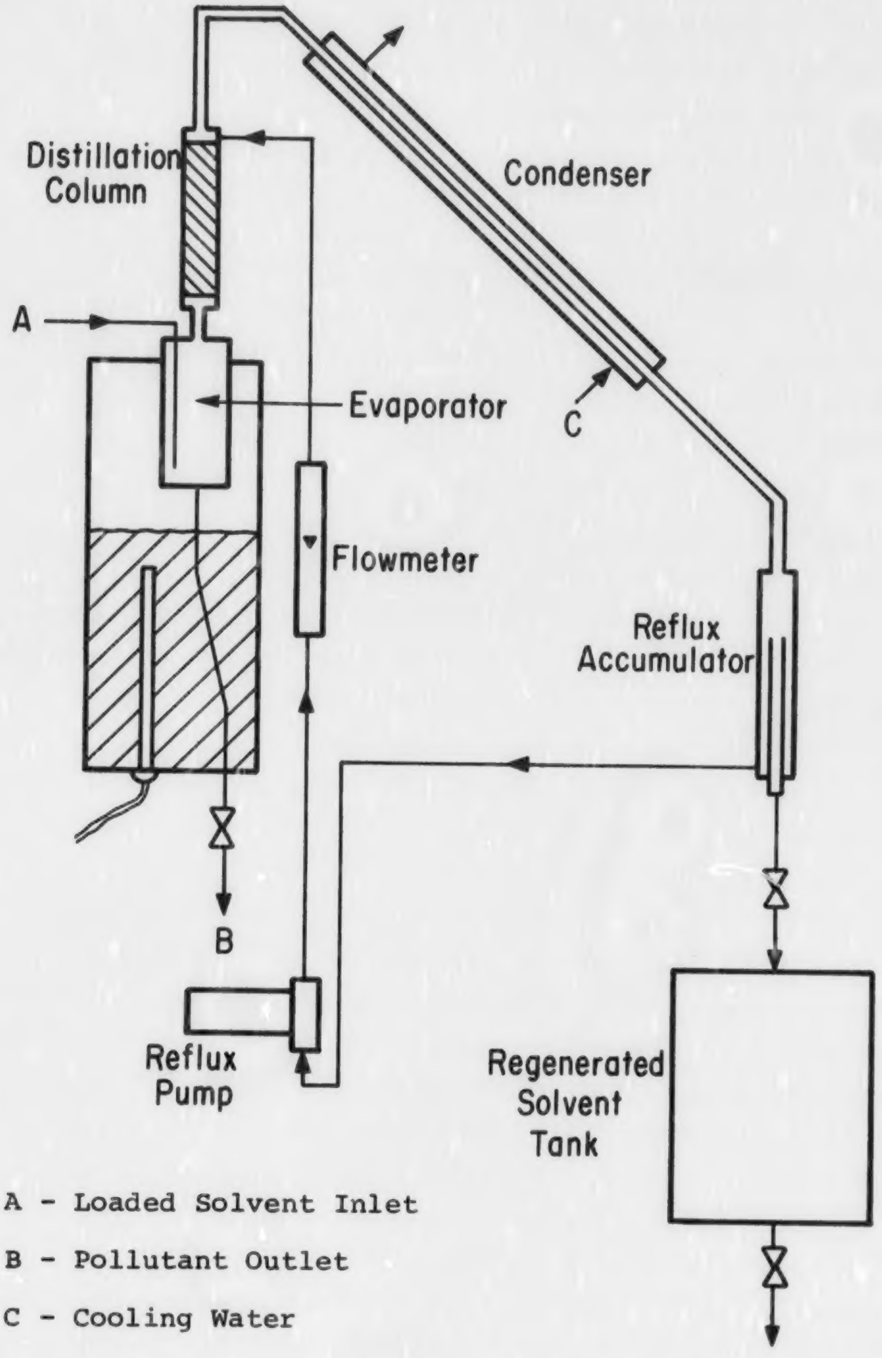
Figure 19. Upper Part of RDC

flowed through a 1/4 inch stainless steel tubing which extended downward to a position about 1 inch above the top disc. A 1/16 inch diameter sample line also extended downward from the top end plate, allowing the aqueous phase to be sampled just below the interface.

Solvent Regeneration Apparatus.

The apparatus used for the regeneration of pollutant-loaded, volatile solvent included an evaporator, a packed distillation column, a condenser, a small reflux accumulator, and a reflux pump arranged as shown in Figure 20. The equipment was designed for a solvent flow rate of 3.4 gal/hr and was thus oversized for the experiments using a low solvent-to-water flow ratio. The regeneration of less-volatile, polar solvent loaded with extracted pollutants was carried out separately in an atmospheric batch distillation apparatus.

The evaporator design took into account the need for keeping unevaporated pollutants in the liquid state before they are withdrawn, as well as the need for variable and controlled temperature differences between the heating medium and the evaporating solvent. The loaded solvent was evaporated in a cylindrical, vertical copper tube about 3 inches in diameter and 12 inches in length as shown in Figure 21. The heat of vaporization was supplied by a double-boiler arrangement, wherein hot Freon-114 vapors were condensed onto the outside of the tube wall. The Freon-114 was in turn evaporated by a 1000 watt electrical heating element (Chromalox Model R1-1100) located inside

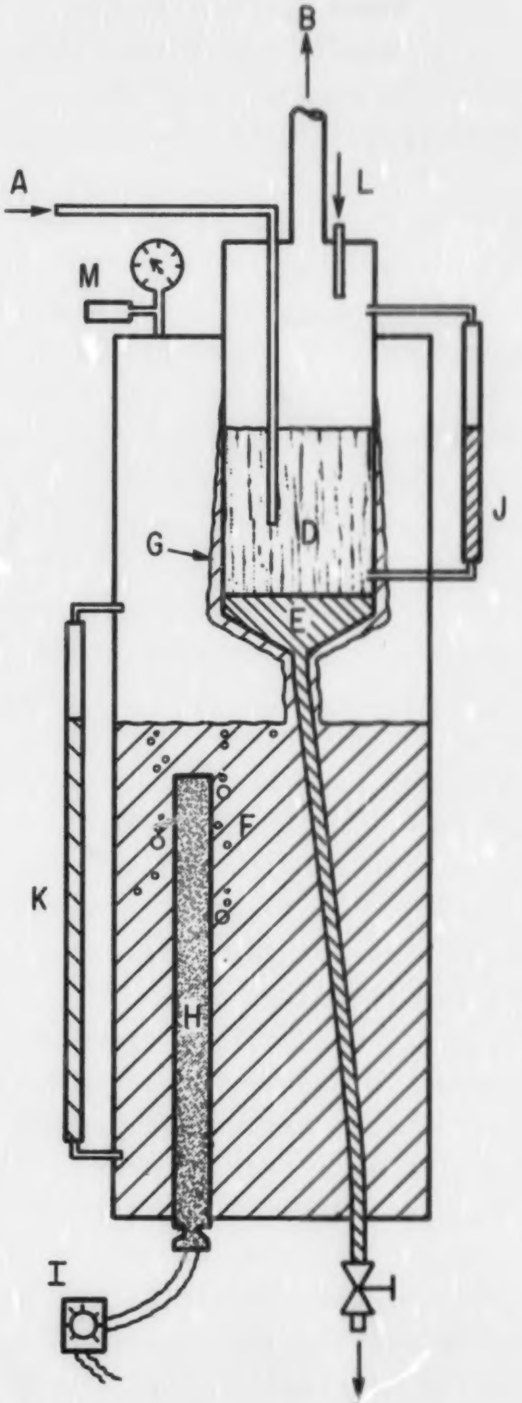


A - Loaded Solvent Inlet

B - Pollutant Outlet

C - Cooling Water

Figure 20. Volatile Solvent Regenerator



A - Pollutant-loaded Solvent

B - Purified Solvent Vapor

C - Pollutant Residue Drain

D - Boiling Solvent

E - Concentrated Pollutant

F - Boiling Freon 114

G - Condensing Freon 114

H - Electrical Heater

I - Heater Power Control

J - Solvent Level Gauge

K - Freon 114 Level Gauge

L - Temperature Well

M - Freon Pressure Gauge and Relief Valve

Figure 21. Miniplant Evaporator

a second, outer container, which surrounded the lower 9 inches of the inner tube. The pressure, and hence the condensation temperature, of the Freon-114 could be varied by adjusting the power input to the heater. The Freon-114 was charged after thoroughly evacuating and flushing the outer container, and since the vapor pressure at room temperature is about 20 psig, no inert gas could enter the evaporator. The concentrated pollutants were intermittently withdrawn through a line at the bottom of the inner evaporator tube. The temperature of the solvent vapors leaving the evaporator was measured by a thermistor in a copper temperature well.

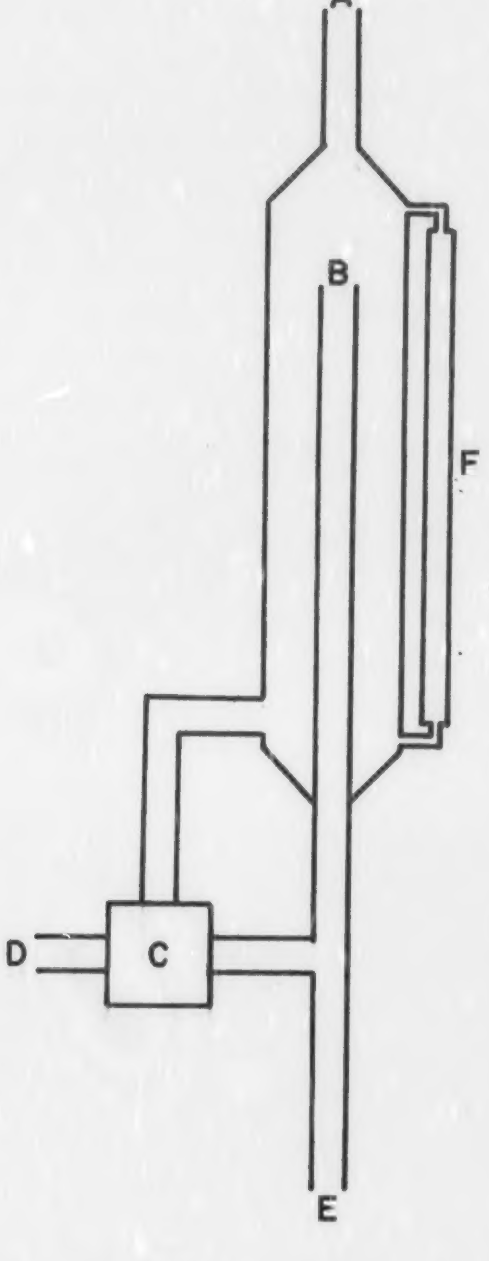
A 12 inch long by 2 inch diameter distillation column packed with 1/4 inch ceramic Raschig rings was mounted on top of the evaporator. The packing was supported by a screen at the bottom, and the liquid reflux was distributed over the top of packing through 5 holes of 0.014 inch diameter. The distillation column was covered on the outside by foam rubber insulation.

The purified volatile solvent vapor leaving the distillation column was condensed in a double-pipe heat exchanger, using chilled water as coolant. The heat transfer surface was a 30 inch length of 1 inch diameter copper water pipe mounted at a 45 degree angle, giving an inside surface area of 0.67 sq. ft. Because of space limitation, chilled water (about 2°C), rather than normal cooling water, was circulated through the jacket of this small condenser to provide the required rate of heat transfer while maintaining the pressure of the condensing solvent below the safe operating pressure of the glass extraction column.

The condensed solvent flowed by gravity into the reflux accumulator shown in Figure 22. The accumulator consisted of a 3/4 inch diameter copper tube inside a 2 inch diameter copper pipe connected so that the annular area between tubes acted to store about 0.12 gal of liquid and so that the inner tube acted as a weir allowing the overflow to pass downward to the regenerated solvent tank. A three-way ball valve arrangement allowed the accumulated liquid to be emptied into the receiving tank if it became contaminated with pollutant (e.g., during startup).

A diaphragm metering pump (Lapp Pulsafeeder, Model LS-10) with a very precise flow rate adjustment was used to pump reflux liquid up through a rotameter, through a flow restriction, and into the distillation column at flows up to 0.61 gal/hr. Because of the pulsating flow, the rotameter was used only to check for proper operation; the flow rate was determined from a separate calibration of the pump control. A flow restriction consisting of a 3/4 inch length of 0.012 inch diameter tubing had to be installed between the reflux pump and the distillation column to eliminate vaporization in the pump. The pump was located about 2 feet below the reflux accumulator to provide the necessary suction head.

Figure 23 is a photograph of the entire mini-plant. The RDC is located at the left, and the other equipment is arranged as in Figure 20. The dark colored tank below and just to the right



A = From Condenser

B = Weir

C = 3-Way Ball Valve

D = To Reflux Pump

E = To Solvent Tank

F = Level Gauge

Figure 22. Reflux Accumulator

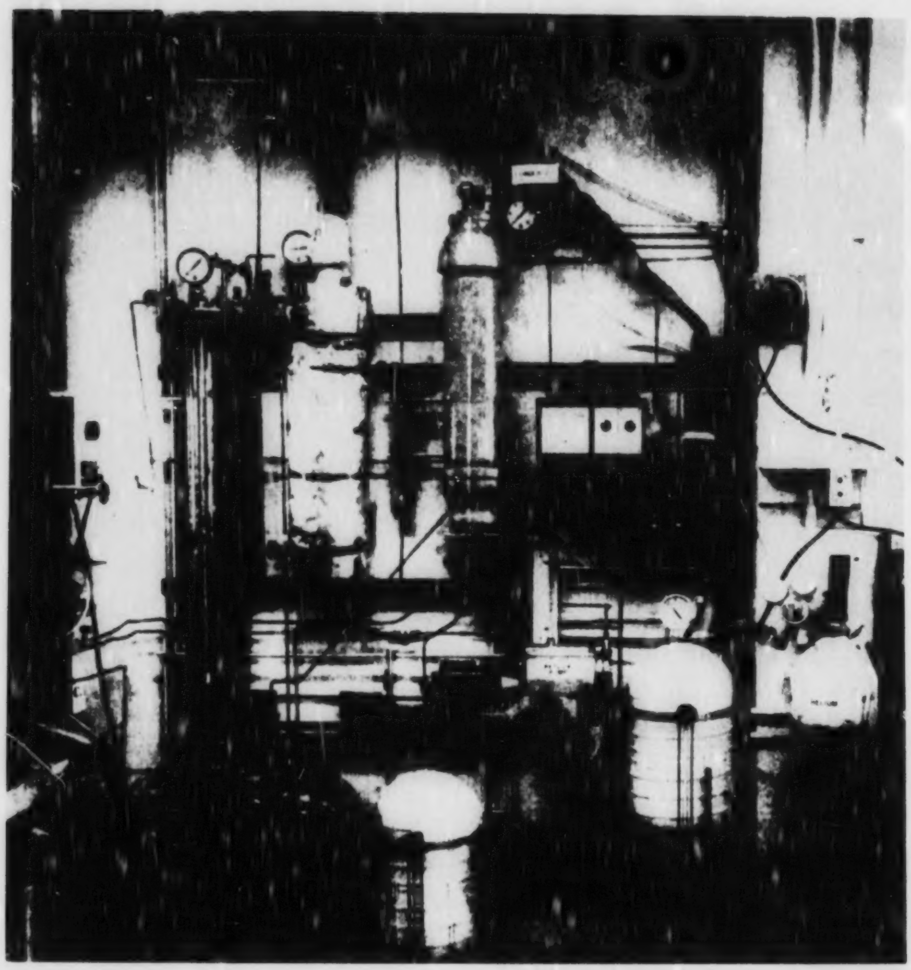


Figure 23. Photograph of Entire Miniplant

of the RDC is a 9-gallon water feed tank; the light colored tank beside it is a 9-gallon volatile solvent feed tank. Helium pressure was applied above the liquids in the two feed tanks to force the fluids to flow up through the equipment thus avoiding the need for feed water and feed solvent pumps. The other 9-gallon, light colored tank is the regenerated solvent tank. The vertical pipe just below the condenser was used as a 4-gallon feed tank for the polar solvent experiments. The instrument just to the right of this pipe tank is an Atkins (Model 3L01J) thermistor reader which was used to display the temperature measurements at the top and the bottom of the extractor and at the vapor outlet of the evaporator.

The pollutant-loaded polar solvent solutions were not regenerated in the mini-plant because the Freon-114 in the evaporator did not provide a high enough temperature. This separation was made in an atmospheric batch distillation apparatus consisting of a 3 liter spherical glass boiling flask driven by an electrical heating mantle, a vertically mounted Allihn condenser which provided reflux by circulation of air through the jacket, and a water cooled Claisen head condenser.

Chemicals Used.

Volatile solvents were purchased from Matheson Gas Products in pressure cylinders. C.P. grade isobutylene of 99.0% purity was found by gas chromatographic analysis to contain about 0.04% of a heavy oil (probably diisobutylene and higher polymerization products) and about 0.01% of tertiary-butanol (the product of reacting water with isobutylene). Instrument grade isobutane of 99.5% purity did not contain any detectable impurity which could be extracted by water (such as t-butanol) or separated by the miniplant distillation (such as heavy oil). The isobutylene was purified before use by running it through the miniplant using pure water to wash out water soluble impurities and the distillation to separate the heavy components. This purification was necessary only because the impurities could interfere with the analysis of some pollutants and because we wanted to test for solvent degradation which might occur during an extraction experiment. Such impurities in the make-up to a commercial installation would cause no problem.

The n-butyl acetate used as a polar solvent was purchased in two qualities: (1) purified grade (Baker Chemical Co.), which contained 0.76% n-butanol as the only appreciable impurity, and (2) technical grade (Bryant Lab, Inc.), which contained 8.26% n-butanol plus at much lower concentrations several other impurities which appeared to be a higher molecular weight ester and several low molecular weight alcohols. The purified grade n-butyl acetate was used without purification because the n-butanol did not interfere with pollutant analyses in those experiments. The technical grade solvent was purified by washing with water in the RDC at a high water-to-solvent flow ratio, followed by a batch distillation. The early fraction from the batch distillation was rewashed in a separatory funnel with water, then added back to the distillation apparatus. The final product from this treatment contained about 0.2% n-butanol and almost no low-boiling impurities, but still contained about 1% of a higher molecular weight ester. The presence of 8% n-butanol in the make-up solvent used in a commercial installation could cause a problem if the rate of solvent loss were high, but the steady state concentration of n-butanol in the solvent would be low because it would be washed out in the purified water.

The 2-ethyl hexanol used as a polar solvent was practical grade (Matheson, Coleman, and Bell), which contained less than 0.2% total impurities; it was used without purification. The n-pentane used in batch extractions was spectroquality (Matheson, Coleman and Bell) of greater than 99% purity and was used as purchased.

The various chemicals used to prepare synthetic waste water solutions were reagent grade or purer quality and were used without purification.

Experimental Procedure.

In a typical extraction experiment, whether in the spray column or the RDC and whether using volatile solvent or less-volatile polar solvent, the procedure involved (1) preparing and charging the water and solvent to the feed tanks, (2) initializing flows in a specific manner that would assure smooth operation and rapid approach to steady state, (3) allowing sufficient time to reach steady operation, (4) collecting final samples and recording measured flow rates, temperatures, and pressures, and (5) terminating flows in a manner that would leave all fluids in one or another of the tanks with all other equipment empty. Between experiments all pieces of equipment which were in contact with pollutant-containing fluids were disassembled and cleaned by water or acetone followed by water washing.

The fluid samples were analyzed by gas chromatography, resulting in data on the steady state concentration of each pollutant in the feed and product water, in the feed and product solvent, and (with the RDC) in the water within the column just below the main interface. From the determined flows and concentrations a steady state material balance could be calculated around the extractor. After an experiment, especially if the steady state balance did not check, the volumes and concentrations of the fluids remaining in the tanks would be determined so that a "whole run" material balance could be calculated. This would usually show the location of any error in the "steady state" material balance. Because of the low flow rate of extracted pollutants leaving the bottom of the evaporator, a steady state material balance around the evaporator and distillation column was not possible.

In preparation for an experiment in which a simulated waste water was to be treated, up to eleven 1-gallon bottles were filled with identical, carefully measured amounts of each solute and water. Since the water feed tank did not contain an agitator, these bottles were shaken intermittently for several hours to assure complete dissolution, and then about nine gallons were added to the water feed tank. When industrial waste water was to be treated, the preparation depended on the type of water. Waste water from lube oil refining was filtered through a coarse filter paper to remove large solid particles which could plug valves and rotameters, its pH was adjusted to about 5, and it was added to the feed water tank. Waste water from cresylic acid recovery was also prepared in this manner. With the ethylene quench water, the aqueous phase was separated from floating and settled organic phase by syphoning through a tube submerged in the sample bottle. Waste water from the oxychlorination plant was neutralized with $NaHCO_3$, as described in Section V.

Before filling the feed water tank with the waste water, it was washed with and then filled with pure water. After pressurizing the feed water tank with helium, the pure water was used to fill the extraction column, thus purging the air from it. When a volatile solvent was to be used, about 500 cc of volatile solvent liquid was then added to the extractor while allowing some water to be displaced out the water-phase outlet line. When a polar solvent was to be used, a low-pressure dry nitrogen line was connected through the solvent outlet line to pressurize the column. Then, under the pressure of volatile solvent vapor or dry nitrogen, about three-quarters of the water in the column was removed and discarded. The volume of the remaining water was recorded for use in calculating the whole run material balance.

The volatile solvent was charged to the solvent feed tank as a liquid by inverting the high pressure cylinder so that its valve was below the level of the liquid in the cylinder. Prior to transferring the solvent, the solvent feed tank was evacuated to about 1 mm Hg absolute pressure, and dry nitrogen was added to the high pressure cylinder to provide a pressure driving force. When a mixture of volatile solvent and less-volatile, polar solvent was to be used, the solvent feed tank was first evacuated, polar solvent was sucked in, and then volatile solvent was added. After both types of solvent had been added, the valves on the tank were closed, and it was shaken by hand to assure thorough mixing.

After the feed tanks were filled with waste water and solvent and were pressurized with helium, the extraction column was filled with waste water to within about 2 inches of the top. Solvent was then added to fill the column completely with liquid. This method of filling the extractor resulted in a concentration gradient at the beginning of an experiment and thus decreased the amount of time required to reach steady state.

The flow rates of both water and solvent were next determined. With the solvent inlet and outlet valves closed, the water flow was started and controlled to the desired setting on the water rotameter by adjusting the water outlet valve. A volume of water was then collected during a timed interval to establish the polluted water volumetric flow rate which corresponded to the chosen rotameter setting. The solvent inlet valve was opened, and the water inlet valve was closed. The solvent flow was controlled to the desired setting on the solvent rotameter by again adjusting the water outlet valve. As the solvent slowly displaced the water from the column, a volume of the water was collected during a timed interval to establish the solvent volumetric flow rate which corresponded to the chosen rotameter setting.

With both the inlet and outlet solvent valves on the extractor closed, the waste water flow rate was set at the desired value, with the inlet valve completely open and the outlet valve used for control with the flow being measured by the rotameter between the feed tanks and the extractor (Figure 24). The inlet solvent valve was then opened completely, and the outlet solvent valve was opened until the water flow into the column was reestablished. Since the flow of solvent had little effect on the column pressure, this procedure does not change the rate at which water flows out of the column; therefore, the interface was stationary. After about 10 minutes to allow the solvent phase above the interface to come to approximately the steady state concentration, the solvent outlet valve was closed until the interface descended to its desired location. If more than the original 9 gallons of waste water was required to complete the run, all flows were stopped at this point,

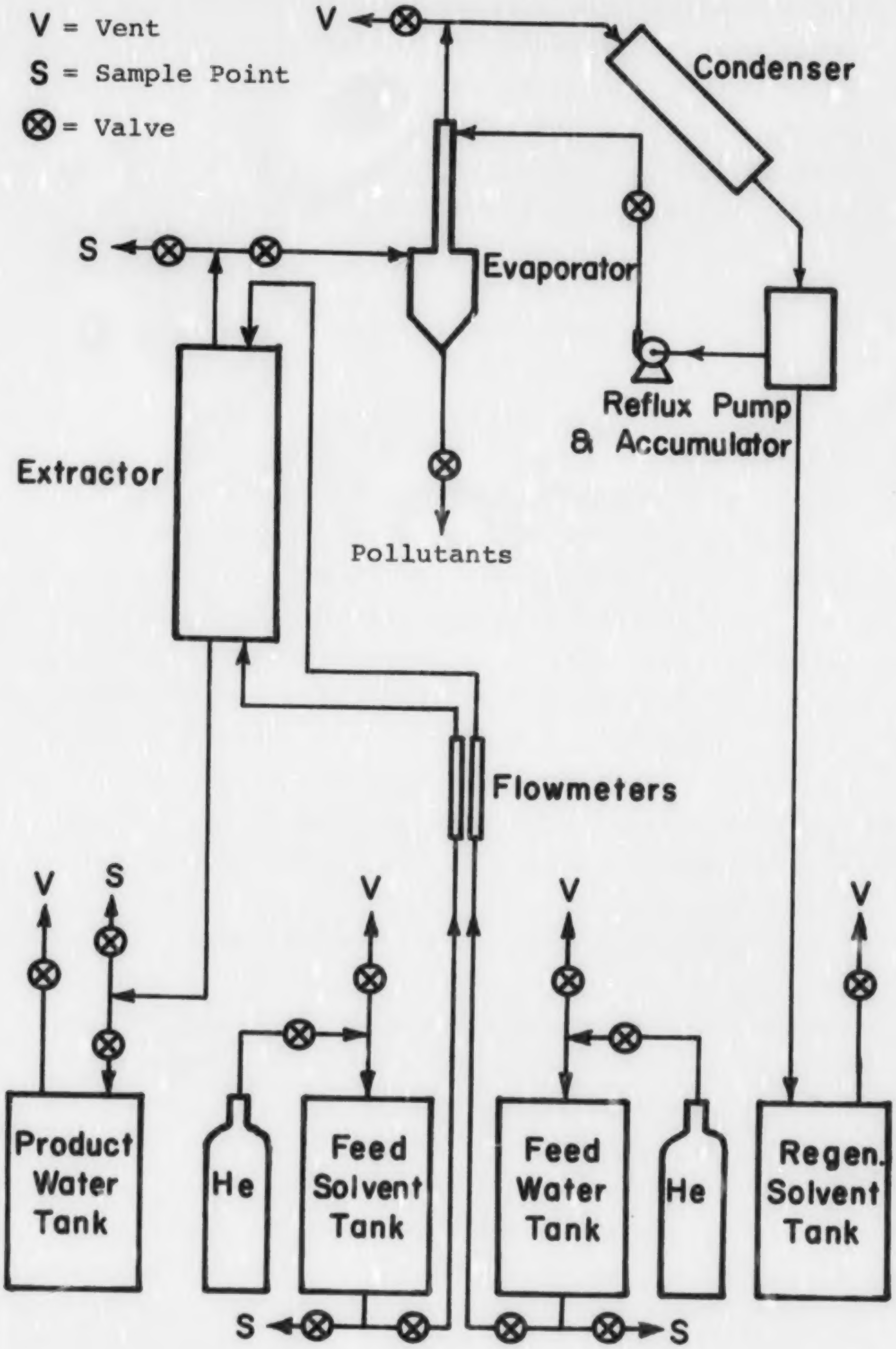


Figure 24. Pilot Plant Flow Diagram

and the water feed tank was refilled. The above precedure was then used to restart the flows. By adjusting the water inlet and solvent inlet valves and then reestablishing the water inlet flow to the desired value by adjusting the solvent outlet valve, any combination of solvent and water flows could be set and still give a stationary interface.

Before starting an experiment in which volatile solvent was used, some pure volatile solvent was passed through the column while it was filled with pure water, and the reflux accumulator was filled with pure liquid volatile solvent by boiling it in the evaporator and condensing it in the condenser. Then, just before the pollutant-containing volatile solvent was first admitted to the evaporator, the reflux pump was started and the evaporator heater activated. When this method was used, the only adjustment that had to be made when the outlet solvent valve on the extractor was opened was to increase both the heater power and the cooling water flow rate.

Once the apparatus was running, the only adjustments necessary were to keep the solvent and water flow rates constant by controlling the solvent outlet valve and to keep the pressure in the condenser constant by adjusting the heater power. The approach to steady state was followed by sampling the water outlet and analyzing for the pollutant concentrations with the gas chromatograph. Steady state operation usually required about 45 minutes, and the equipment could be operated for at least 30 additional minutes before the feed water tank was emptied. During this period the pollutants which accumulated in the evaporator were intermittently withdrawn out the bottom and were collected in a previously weighed pressure vessel of about 500 ml volume.

After steady state was attained, final samples were taken of the outlet water, the outlet solvent, and (with the RDC) the water within the column. The solvent inlet and water outlet valves were then closed until the interface ascended to just below the top of the column, at which time the solvent outlet valve was closed. The column was then drained into the water receiving tank, a glass carboy located within a fume hood to eliminate the solvent vapors that were released when the pressure was decreased across the water outlet valve. The evaporator was allowed to run until no more liquid was present in the evaporation tube at which time the reflux pump was stopped, the heater turned off, the condenser water flow stopped, and the reflux accumulator drained into the regenerated solvent tank.

After the run, the total quantity of water treated was determined by measuring the volume of the accumulated purified water and subtracting the volume of the pure water initially present in the column. The total quantity of solvent used was determined from the volume in the regenerated solvent tank. The total quantity of concentrated pollutant residue was determined by weighing the collecting vessel. After the concentrations of pollutants were determined in these liquids, the whole run material balance was readily calculated.

SECTION VII

SPRAY COLUMN - EXPERIMENTAL RESULTS

The primary objective of experiments conducted in the spray column was to prove the overall process feasibility of volatile solvent extraction. The majority of runs were conducted with isobutylene as the dispersed phase; however, for comparison water was dispersed into isobutylene in several runs, and n-butane was dispersed in one experiment. A variety of types of organic chemicals was extracted, including one aromatic hydrocarbon (benzene), two alcohols (n-butanol and isoamyl alcohol), two esters (vinyl acetate and n-butyl acetate), two ketones (acetone and methyl ethyl ketone), one aldehyde (crotonaldehyde), one nitrile (propionitrile), one chlorinated hydrocarbon (ethylene dichloride), and several phenolics (phenol; o-cresol; m, p-cresol; and xylenols). Most of these solutes are known to be present in the waste water from chemical processing plants, but they were also chosen to determine if any class of organic chemicals might cause unexpected problems such as an irreversible reaction with isobutylene. Most of the solutes studied were present in synthetically prepared water solutions, but samples of lube oil refining waste water and cresylic acid recovery waste water were also tested. Many more industrial waste waters were tested with the RDC extractor (see Section VIII).

Each experiment was conducted in the miniplant spray column extractor as described in Section VI. In addition to the types of solutes and the choice of volatile solvent, the principal independent variables were the water and solvent flow rates. The temperature was measured but not controlled. The principal measured response was the concentration of each solute in the product water. Approximate measurements were made of the droplet size, by holding a scale against the glass column, and of the time for a droplet to travel from the distributor to the main interface, by using a stopwatch. From the "whole run" material balance (see Section VI), it was possible to estimate the effectiveness of solvent regeneration. However, the procedure for sampling and analyzing the pressurized solvent was not perfected until after the experiments in the spray column had been completed.

In this chapter we first describe the method of reducing the data on solute removal efficiencies to mass transfer coefficients. A sample calculation is described for Run SS12A (SS = Spray column with Solvent dispersed; 12 = sequence number; and A = first setting of solvent and water flow rates). The correlations which describe the hydrodynamics and axial mixing in the spray column are shown to provide a reasonable description of its operation. The mass transfer models for circulating and oscillating drops are shown to bracket the experimental results for Run SS12A.

The experimental results are then described and discussed with respect to answering such questions as which phase should be dispersed and when are solute interactions important. The results from several experiments indicate that the solvent phase rather than the aqueous phase should be dispersed. Experiments in which the performance using n-butane as solvent was compared to the performance using isobutylene show that isobutylene is usually preferred. Isobutylene tends to give both higher distribution coefficients and higher mass transfer coefficients. While experiments did not lead to a clear understanding of interactions between solutes, the results did indicate that such interactions can be important. Mass transfer rates were often found to be higher than theoretically predicted for oscillating drops as well as for circulating drops. Runs are described in which lube oil refining waste water and cresylic acid recovery waste water were treated by volatile solvent extraction. Further details on the method of data reduction along with a listing of the computer program used to make the calculations and the experimental results for all 37 runs conducted in the spray column are listed in Appendix G.

Method of Data Reduction.

Although the comparison of solute removal efficiencies is a useful means of comparing various modes of operation, a better comparison is possible in the spray column experiments by reducing the data to mass transfer coefficients (or equivalently, numbers of transfer units) and then by comparing these to theoretical and empirical predictions. This procedure requires the use of the design methods described in Section V and Appendix B to predict the effects of hydrodynamics, axial mixing, and mass transfer rates. The procedure of data reduction is described for Run SS12A, an experiment in which a prepared waste water containing about 2000 ppm each of acetone and n-butyl acetate and about 4000 ppm each of methyl ethyl ketone (MEK) and crotonaldehyde was treated with isobutylene as the dispersed phase.

Estimation of physical properties. The estimation of solvent droplet size and solvent holdup requires data on the densities of both phases, on the interfacial tension, and on the aqueous-phase viscosity. In addition, for estimation of mass transfer rates, data are required for the solvent viscosity and the diffusivities of each solute through water and through isobutylene. The values used at the measured temperature of 21.6°C are listed in Table 8. The aqueous-phase density and viscosity were taken as those listed by Weast (1970) for pure water. The density of the solvent phase was taken to be that of pure isobutylene (API, 1963), and the solvent-phase viscosity was estimated by extrapolating low-temperature (-110°F to +10°F) viscosity data for n-butane, iso-butane, and 1-butene (API, 1963) and assuming that the viscosity of isobutylene is the product of the viscosity of 1-butene and the ratio of viscosities of iso-butane to n-butane. The interfacial tension was estimated by plotting data for several hydrocarbons for which data is available (n-pentane, n-hexane, n-heptane, and n-octane) in the manner suggested by Donahue and Bartell (1952). These authors showed that the interfacial tension of many systems fell on a single line when plotted as

Table 8. Physical Properties for Run SS12A

Continuous-phase density = 0.9979 gm/cc

Continuous-phase viscosity = 0.9704 cp

Dispersed-phase density = 0.5914 gm/cc

Dispersed-phase viscosity = 0.182 cp

Interfacial tension = 41.5 dyne/cm

Solute diffusivities (10^5 x ft^2/hr) and distribution coefficients:

Solute	D_c	D_d	K_d
Acetone	4.22	26.2	0.63
MEK	3.87	24.0	2.49
Crotonaldehyde	3.88	24.0	2.48
n-Butyl Acetate	2.71	20.4	168.

interfacial tension vs. the logarithm of the sum of mole fraction solubility of water in the organic-phase and mole fraction solubility of the organic in water. The mutual solubilities for the hydrocarbon-water binary systems were taken from API (1963). The diffusivities were estimated as recommended by Reid and Sherwood (1966) using the method of Scheibel (1954) and assuming that the values at infinite dilution would apply at the low concentrations in the experiment. The distribution coefficients were taken from Appendix E assuming the values at 25°C and at infinite dilution would apply.

Estimation of hold-up and Peclet number. In Run SS12A the isobutylene flow rate was 21.3 gal/hr which when passed through the 30 holes of 1/16-inch diameter in the distributor gave a discharge velocity of 0.1236 ft/sec. Since this is considerably less than the jetting velocity of 1.12 ft/sec predicted by the method of Scheele and Meister (1968), their correlation could reliably be used to estimate the average drop size of 0.1819 inch. This agreed very well with estimates made by visual observation. By using the correlation of Minard and Johnson (1952), operation during this run was estimated to be 11.9% of flooding (i.e., 11.9% of the fluid velocities at flooding with the same ratio of phase flows). The method of Hughmark (1967) was used to estimate the hold-up as $\phi = 0.0272$, and the correlation of Henton, et al. (1973) predicted $Pe_c = 2.017$ as an estimate of axial mixing. Assuming the velocity of the rising droplets to be V_d/ϕ leads to a rise time of 6.6 sec which agrees with an average experimental estimate of 7 sec.

Circulating-drop estimate of mass transfer. Using the estimates of droplet size and hold-up, the correlation of Ruby and Elgin (1955) was used to estimate k_c for each solute, and equations (5) and (B5) were used to calculate N_c ($=N_w$). The dispersed-phase mass transfer coefficient for circulating drops was estimated by the equation of Kronig and Brink (1950) which assumes no resistance to mass transfer in the continuous phase. In Run SS12A the water flow rate was 0.948 gal/hr, which when combined with the solvent flow rate and the two fluid densities led to $F_s/F_w = 1.331$, from which the value of E for each solute was determined. The predicted values of N_w and N_s were then combined according to equation (4) to give the predicted value of N_{ow}. The results of these estimates are listed in Table 9 and plotted as the upper curve on Figure 25. R ($= k_c/k_d K_d = N_w/N_s E$) is also included in Table 9.

Oscillating-drop estimate of mass transfer. A similar procedure was followed using the equations of Angelo, et al. (1966; 1968) for oscillating drops; these results are also listed in Table 9 and plotted as the lowest curve on Figure 25. The major factor increasing the rate of mass transfer for oscillating drops relative to circulating drops is a 3- to 5-fold increase in N_s.

Experimental mass transfer results. To compare the experimental results with the predictions for circulating drops and for oscillating drops, the removal efficiency data were corrected for end

Table 9. Predicted Mass Transfer Rates

	Acetone	MEK	Crotonaldehyde	n-Butyl Acetate
E	0.84	3.31	3.30	224.
Circulating Drops:				
N_w	2.46	2.34	2.35	1.90
N_s	0.61	0.58	0.58	0.54
N_{ow}	0.42	1.06	1.06	1.87
R	4.8	1.2	1.2	0.016
Oscillating Drops:				
N_w	2.84	2.72	2.73	2.28
N_s	3.15	3.02	3.02	2.78
N_{ow}	1.37	2.14	2.14	2.27
R	1.1	0.27	0.27	0.004

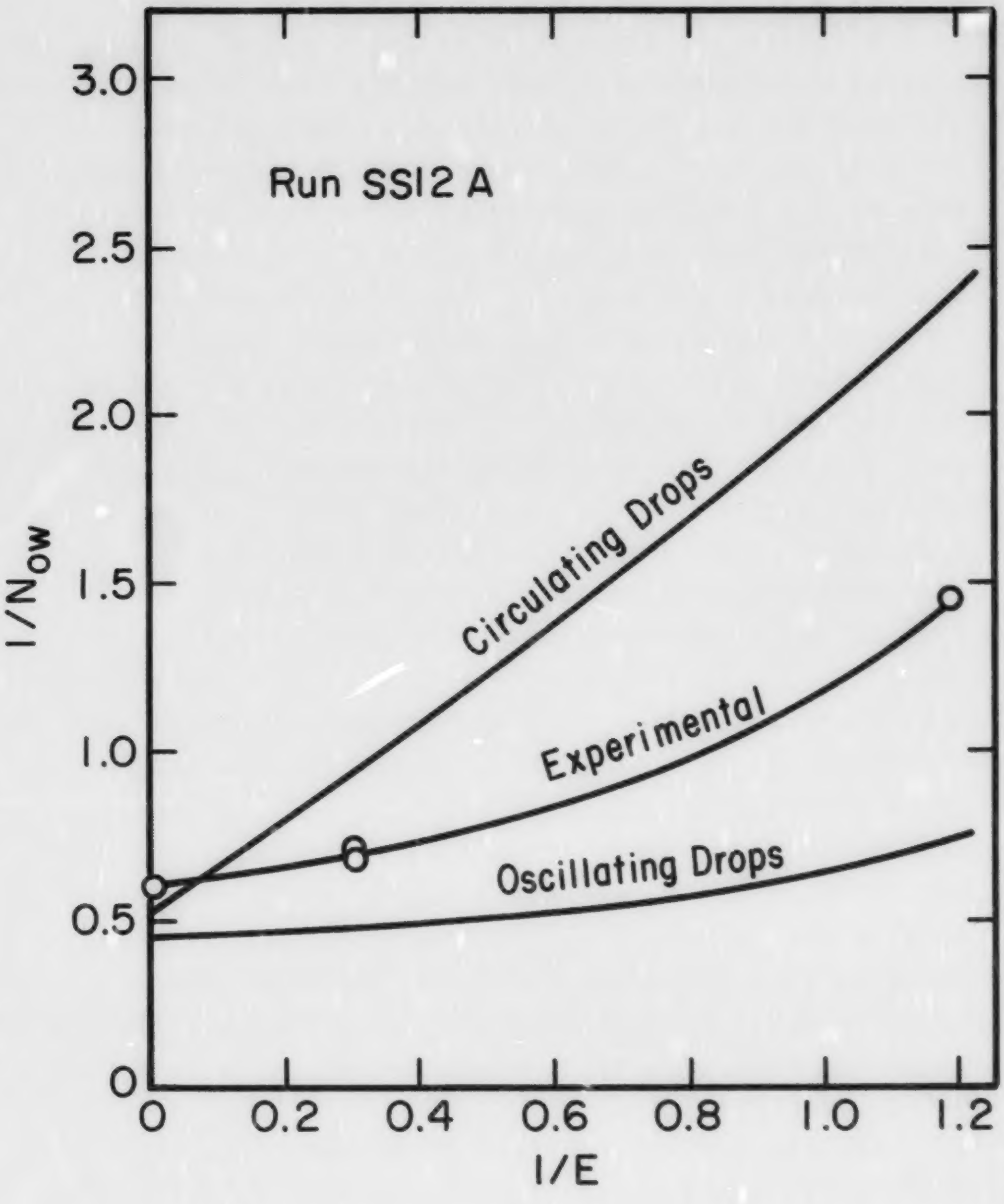


Figure 25. Mass Transfer Rates

effects and converted to values of N_{ow}. In using equation (14) to correct for mass transfer during solvent droplet formation, the continuous-phase concentration was assumed to be the measured outlet aqueous-phase concentration, and the feed solvent was assumed to be free of solutes. The correction for mass transfer during water droplet formation was made by assuming the continuous solvent-phase concentration was that which would satisfy a material balance around the spray column. The corrections for mass transfer during droplet coalescence were made assuming the continuous-phase concentration was the feed concentration (i.e., neglecting the concentration jump) and assuming the dispersed-phase concentration was the concentration of the product. The measured (before drop formation and after drop coalescence) and corrected (for end effects) aqueous-phase concentrations which are listed in Table 10 show that these corrections are relatively minor, which justifies the approximate nature of the corrections. The corrected concentrations were used to calculate η according to equation (1). Using the previously estimated $Pe_w = 2.017$ and assuming that Pe_s is infinite, equation (3) was solved implicitly to give the values of N_{ow} for each solute as listed in Table 10 and plotted on Figure 25. The experimental results fall between the curves for oscillating drops and for circulating drops for all solutes except n-butyl acetate.

All the curves in Figure 25 deviate from straight lines which would occur if the values of N_w (and N_s) were the same for each solute. The prediction

Table 10. Experimental Mass Transfer Rates

	Acetone	MEK	Crotonaldehyde	n-Butyl Acetate
Ppm in Feed Water	2058	4167	4422	2212
Ppm Corrected* Feed	2038	4078	4328	2150
Ppm in Product Water	1307	1579	1620	620
Ppm Corrected* Product	1329	1621	1663	637
Ppm in Feed Solvent	0.0	0.0	0.0	0.0
Ppm Corrected* Solvent	16.6	31.3	32.1	13.0
η	0.648	0.396	0.382	0.296
Experimental N_{OW}	0.69	1.40	1.48	1.68

* for end effects

for circulating drops shows curvature because of differences in solute diffusivities. Additional curvature would have been introduced had the correction to additivity of the individual-phase resistances been included in the predicted curves. The correction due to the interaction of resistances is largest at R=1 and falls to zero at large and at small values of R. The point R=1 occurs near 1/E=0.25 for the circulating drop model and near 1/E=1.1 for the oscillating drop model. The corrected curves would lie slightly below those plotted, following results presented by King (1965) for various simplified models. The curvature in the prediction for oscillating drops is due to variations in solute diffusivities. The fact that the experimental line shows curvature like that for the oscillating drops does not necessarily mean this model is most representative.

Because of the complex nature of these calculations, it is not readily apparent how errors in the assumed values of physical properties will influence the comparison between experimental and predicted values of N_{ow}. It is unlikely that the estimates for densities or viscosities are much in error, but the interfacial tension could be substantially reduced by the presence of the solutes and other impurities. If the interfacial tension were 20.0 dynes/cm rather than 41.5 dynes/cm, the solvent hold-up would be increased from 0.0272 to 0.0314, and the average droplet diameter decreased from 0.1819 inch to 0.1494 inch. These changes would result in the increased rate of mass transfer for both circulating and oscillating drops shown by the dashed lines in Figure 26. The increase in estimated hold-up would result in an increase in Pe_c which causes a slight change in the experimental curve. The estimated values of the solute diffusivities could also be in error. Reid and Sherwood (1966) found when using the Scheibel method that the average error for the diffusivity of organics in water was 11% and for the diffusivity of organics in other organic solvents was 25%. The vertical bars on the predicted curves in Figure 26 show the range of changes in N_{ow} caused by an 11% increase in all values of D_c and a 25% increase in all values of D_d or by an 11% decrease in D_c's and a 25% decrease in D_d's. Changing diffusivities has almost no effect on the experimental curve since they only enter into the minor correction for end effects. Figure 26 shows that these errors in physical properties would not change the location of the experimental curve from that of lying between the curves for circulating drops and for oscillating drops.

Choice of Dispersed Phase.

The results of Runs SS11 and SW3 give some insight into how operation with isobutylene dispersed compares with operation with water dispersed. In both these experiments a single solute, ethylene dichloride (measured $K_d = 70.0$, by the method reported in Appendix E), was present in the feed water at about 3000 ppm. When isobutylene was dispersed in two experiments in which the water flow rate was held constant at 1.50 gal/hr, the removal efficiency decreased from 87.2% with an isobutylene flow rate of 1.76 gal/hr to 62.0% with an isobutylene flow

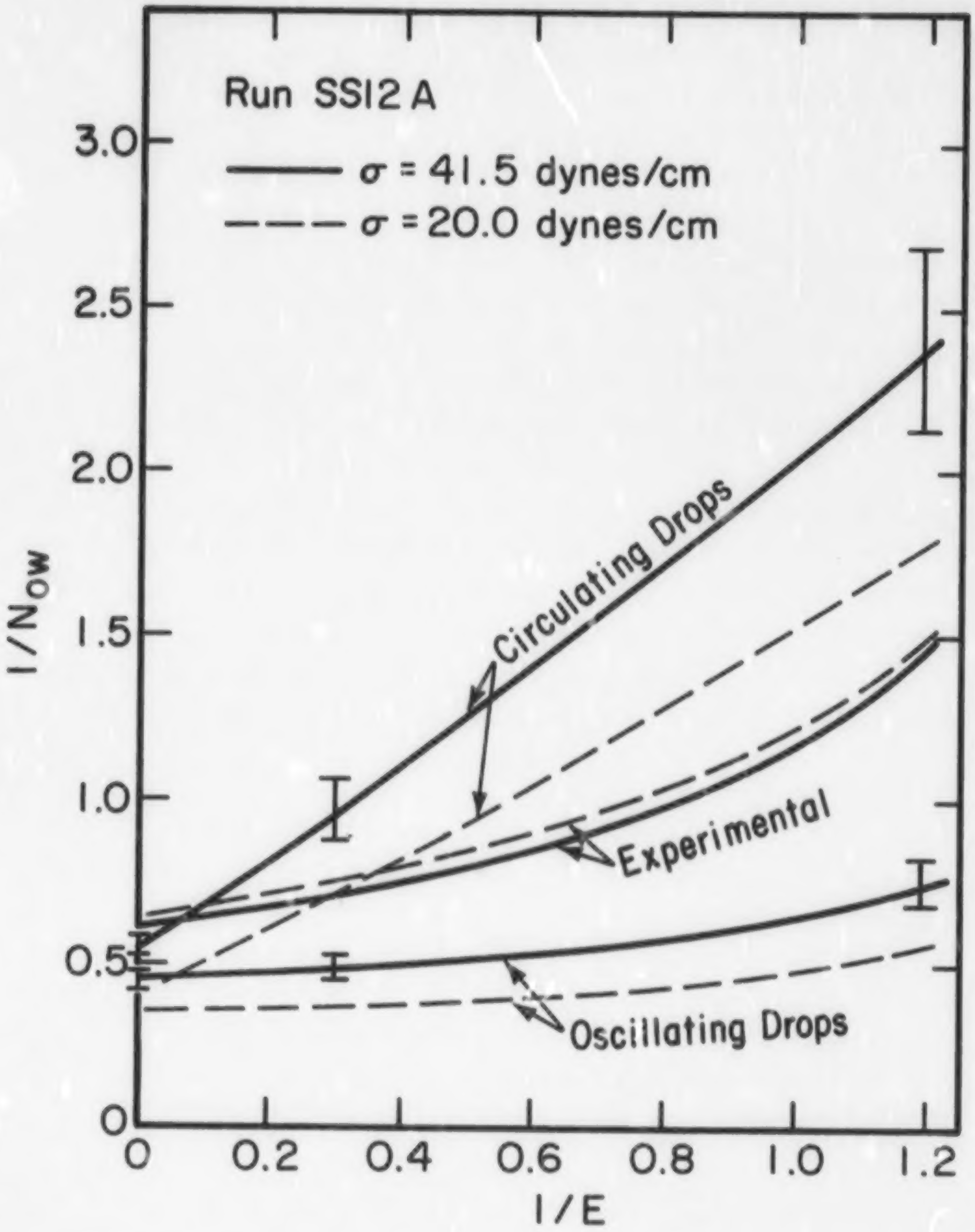


Figure 26. Effect of Physical Properties

rate of 0.700 gal/hr. This decrease must reflect a decrease in $k_c a$ since the major resistance to mass transfer is in the water phase. The main reason for this decrease is the decrease in solvent hold-up and therefore in a. The results of comparing the experimental with the predicted values for N_{ow} are shown in Table 11. For Runs SS11A and SS11B the experimental N_{ow} was larger than the prediction for oscillating drops as well as that for circulating drops, but the ratio of experimental N_{ow} to predicted N_{ow} for oscillating drops was constant at about 2.2 for these two runs.

When water was dispersed into isobutylene at five different flow settings in Run SW3, the ethylene dichloride removal efficiency ranged from 51 to 55% and was nearly independent of solvent flow rate; it showed only a slight variation with water flow rate. Since the resistance to mass transfer was almost entirely in the water phase, the solute removal efficiency from a droplet of water falling through the solvent is expected to be only slightly affected by the solvent flow rate. When the water flow rate was decreased, the droplet size decreased slightly which accounts for a slightly improved removal efficiency. The results of comparing the experimental with the predicted values of N_{ow} are shown in Table 11; they indicate that the experimental N_{ow} fell between the values predicted for circulating and for oscillating drops. The ratio of experimental N_{ow} to N_{ow} predicted for oscillating drops ranged from 0.82 to 0.92 for these five runs with the water phase dispersed.

Table 11. Comparison of Runs with Different Phases Dispersed

(Solute = Ethylene Dichloride)

Run #	V_w (ft/hr)	V_s (ft/hr)	E	Pe_c	% Removal	N_{ow} (experimental)	N_{ow} (circulating)	N_{ow} (oscillating)
SS11A	36.8	43.2	48.8	2.93	87.2	3.09	1.15	1.37
SS11B	36.8	17.2	19.4	2.19	62.0	1.24	0.49	0.57
SW3A	36.8	43.2	49.1	2.57	51.1	0.71	0.26	0.86
SW3B	36.8	30.2	34.3	1.79	52.0	0.74	0.26	0.85
SW3C	36.8	17.2	19.5	1.02	50.9	0.72	0.26	0.85
SW3E	27.2	43.2	66.3	2.35	55.4	0.80	0.26	0.88
SW3D	27.2	30.2	46.3	1.64	55.1	0.80	0.26	0.87

Further insight into the question of which phase to disperse was gained from Runs SS9 and SW1. In these runs, isoamyl alcohol (measured $K_d = 3.53$) was present at about 2000 ppm in the feed water in addition to about 3000 ppm of ethylene dichloride. The changes in removal efficiencies with changes in isobutylene flow rate were similar to those in the experiments where only ethylene dichloride was present. However, a comparison of experimental values of N_{ow} with values of N_{ow} predicted for oscillating drops as listed in Table 12 shows that the rate of mass transfer was greater than that predicted for oscillating drops for both water dispersed and solvent dispersed. Comparing the values of N_{ow} for ethylene dichloride with and without isoamyl alcohol being present shows that when the alcohol was present, the rate of mass transfer was increased. This is probably the result of interfacial turbulence being promoted by the presence of the alcohol. The inconsistently high experimental values of N_{ow} in Run SS9C were traced to a sample bottle which did not seal. The product water sample showed a concentration of ethylene dichloride which was too low due to volatilization losses; the loss of isoamyl alcohol was also appreciable but was not as significant as the loss of the more volatile ethylene dichloride.

One additional set of runs was completed with water as the dispersed phase. In Run SW2 about 3000 ppm of ethylene dichloride and about 2000 ppm each of n-butanol (measured $K_d = 0.76$) and n-butyl acetate (measured $K_d = 168.0$) were present in the feed water. The results of a comparison of experimental and predicted N_{ow} are shown in Table 13.

Table 12. Comparison of Runs with Different Phases Dispersed

(Solutes = iso-Amyl Alcohol and Ethylene Dichloride)

Run #	V_w (ft/hr)	V_s (ft/hr)	Solute	E	Pe_c	% Removal	N_{ow} (experimental)	N_{ow} (oscillating)
SS9A	51.3	43.2	IAA	1.76	4.12	71.0	2.28	0.79
			EDC	34.9		92.5	3.96	1.00
SS9B	51.3	30.2	IAA	1.23	3.66	52.7	1.24	0.56
			EDC	24.4		78.1	2.02	0.72
SS9C	51.3	17.2	IAA	0.70	3.07	47.0	1.53	0.33
			EDC	13.9		(98.4)	(9.53)	0.42
SW1B	51.3	43.2	IAA	1.77	2.91	44.0	0.74	0.69
			EDC	35.1		68.9	1.19	0.88
SW1A	51.3	17.2	IAA	0.70	1.15	30.9	0.65	0.68
			EDC	14.0		59.1	0.94	0.87

Table 13. Additional Runs with Water as the Dispersed Phase

(Solutes = n-Butyl Alcohol, Ethylene Dichloride, and n-Butyl Acetate)

Run #	V_w (ft/hr)	V_s (ft/hr)	Solute	E	Pe_s	% Removal	N_{ow} (experimental)	N_{ow} (oscillating)
SW2A	36.8	43.2	n-BuOH	0.53	2.57	25.1	0.47	0.46
			EDC	49.0		82.5	1.80	0.86
			n-BuAc	118.		79.1	1.59	0.75
SW2B	36.8	30.2	n-BuOH	0.37	1.79	23.4	0.61	0.46
			EDC	34.3		80.2	1.69	0.86
			n-BuAc	82.2		75.0	1.41	0.75
SW2C	27.2	30.2	n-BuOH	0.50	1.64	27.0	0.62	0.47
			EDC	46.3		83.0	1.85	0.88
			n-BuAc	111.		78.3	1.55	0.76

Although the theory for oscillating drops (Angelo, et al., 1966 & 1968) has not been well tested, the fact that the experimental values of N_{ow} are larger than predicted for oscillating (as well as for circulating) drops may be another indication of interfacial turbulence.

It is interesting to compare the removal efficiencies of ethylene dichloride and n-butyl acetate in this experiment. Both predicted and experimental values of N_{ow} were larger for ethylene dichloride than for n-butyl acetate, even though the latter had a larger distribution coefficient. The reason for this difference was the larger diffusivity for ethylene dichloride. The extraction factor for both these solutes was so large that almost all the resistance to mass transfer was in the aqueous phase where the diffusivity of ethylene dichloride was predicted to be 3.37×10^{-5} ft^2/hr while that for n-butyl acetate was predicted to be 2.51×10^{-5} ft^2/hr.

These experiments in which the choice of which phase to disperse was considered can now be summarized. For cases where the flow rates of the two phases were about equal, better performance was obtained by dispersing the volatile solvent. The mass transfer rates when the solvent was dispersed were greater relative to predictions for oscillating drops than when the water phase was dispersed. Also, the predictions for oscillating drops were larger with the solvent dispersed, mainly because this mode of operation gave a continuous phase with a much larger viscosity leading to a longer drop residence time.

Since the performance fell less sharply with decreasing solvent flow when the water was dispersed than when the solvent was dispersed, there is likely a lower limiting ratio of solvent to water flow below which dispersing the water will result in a greater solute removal efficiency. However, operation with a very low solvent-to-water flow ratio in the spray column gives poor solute removal efficiencies no matter which phase is dispersed, so other types of extractors would likely be preferred. In general, it appears preferable to disperse the solvent for all modes of operation giving a high removal efficiency.

Choice of Type of Volatile Solvent.

The results from Run SS10 where n-butane was dispersed, when compared to Run SS9 where isobutylene was dispersed, give some insight into the relative merits of these two volatile solvents. In Run SS10 n-butane was used to treat a prepared waste water containing about 3000 ppm of ethylene dichloride (measured $K_d = 44.0$) and about 2000 ppm isoamyl alcohol (measured $K_d = 1.41$); this feed water had nearly the same composition as that used for Run SS9. The predicted values of N_{ow} for oscillating drops are compared to experimental values of N_{ow} for Runs SS10 and SS9 in Table 14. A more detailed study showed that predicted values of N_w were essentially the same for the two volatile solvents, while N_s was about 7% larger for isobutylene than for n-butane. For ethylene dichloride, where the resistance to mass transfer was almost entirely in the aqueous phase, the predicted values of N_{ow} were essentially equal.

Table 14. Comparison of Results When Using Different Volatile Solvents

(n-Butane used in Run SS10; i-Butylene used in Run SS9)

Run #	V_w (ft/hr)	V_s (ft/hr)	Solute	K_d	E	Pe_w	% Removal	N_{ow} (experimental)	N_{ow} (oscillating)
SS10A	51.3	43.8	IAA	1.44	0.68	3.85	42.6	1.10	0.63
			EDC	44.0	20.9		74.6	1.75	1.00
SS10B	51.3	31.4	IAA	1.44	0.49	3.47	29.4	0.61	0.46
			EDC	44.0	15.0		59.1	1.07	0.74
SS10C	51.3	17.4	IAA	1.44	0.27	2.88	19.1	0.41	0.26
			EDC	44.0	8.32		42.7	0.63	0.42
SS9A	51.3	43.2	IAA	3.53	1.76	4.12	71.0	2.28	0.79
			EDC	70.0	34.9		92.5	3.96	1.00
SS9B	51.3	30.2	IAA	3.53	1.23	3.66	52.7	1.24	0.56
			EDC	70.0	24.4		78.1	2.02	0.72

However, for isoamyl alcohol, which had lower values of K_d in both solvents and therefore had a larger resistance to mass transfer in the solvent phase, both the lower K_d and the lower N_s for n-butane as solvent resulted in substantially lower values being predicted for N_{ow}.

The experimental values of N_{ow} in Table 14 show that the factor which was even more significant than a larger value of K_d in isobutylene was the fact that the ratio of experimental N_{ow} to predicted N_{ow} was much larger for isobutylene than for n-butane. Therefore, isobutylene would in general be the preferred choice as volatile solvent. Even for solutes which show a very large value of K_d, the better ratio of experimental to predicted N_{ow} (if this factor occurs for other waste waters) would result in higher removal efficiencies with isobutylene. One factor which does weight in favor of butane in terms of process costs is the lower solubility and lower solvent make-up.

Solvent reactivity could also affect the choice of volatile solvent. In one early experiment (to be described below as Run SS6) in which isobutylene was used to extract phenol from a waste water, a solute was detected in the product water which was not present in the feed water. This solute was identified by chromatographic analysis to be tert-butanol. Since a 2% phenol solution is slightly acidic ($pH \approx 4$) and since isobutylene is known to react with water in acidic media to form tert-butanol, an experimental program was carried out to determine the importance of this reaction.

Isobutylene does not undergo appreciable hydration in 2% phenol solution, and the source of the tert-butanol was found to be the feed isobutylene which contained about 0.01% tert-butanol impurity. However, during the program isobutylene was found to undergo both hydration and dimerization in more acidic solutions. Therefore, butane would be the preferred volatile solvent for the treatment of a waste water which is acidic and which can be reused without neutralization if the organic solutes are first removed. The highly acidic waste water from certain steps in the production of vinyl chloride would be an example of such a waste water.

Interactions Among Solutes.

The previous results showed that the presence of isoamyl alcohol could improve the removal of ethylene dichloride, even though both solutes were present at such high dilution that their values of K_d should equal K_d at infinite dilution. This is an example of solute interactions. A series of experiments was conducted in the spray column extractor to try to improve our understanding of these interactions and also to try to determine under what conditions interactions tend to increase values of N_{ow}.

In this series of experiments two solutes with widely differing values of K_d, acetone with K_d=0.63 and n-butyl acetate with K_d=168.0, (Appendix E), were included so that the relative importance of mass transfer in each phase could be estimated. In Run SS15 about 2000 ppm each of only acetone and n-butyl acetate were present. The results of an analysis of the mass transfer are shown in Table 15. In Run SS15A the experimental values of N_{ow} were much larger than those predicted by the oscillating drop model; the measured removal efficiency for acetone was so large that according to the dispersion model it should not have been possible even with an infinite number of transfer units.

There are several possible explanations for experimentally determined values of N_{ow} being infinite. Had the actual removal efficiency for acetone been 59.4% rather than the measured value of 71.2%, then the experimental value of N_{ow} would have been 4. Although the difference in concentration of acetone in the product water (831 ppm for 59.4% removal, rather than the 590 ppm measured) is much larger than the expected analytical error, acetone could have been lost through vaporization during the short period between when the sample was collected and when it was analyzed by gas chromatography. Another possibility is that the extent of backmixing was overestimated. If $Pe_w = \infty$ (plug flow in both phases), the measured removal would have been possible with $N_{ow} = 3.31$ for acetone and $N_{ow} = 5.15$ for n-butyl acetate. However, even these values are larger than what was estimated for oscillating drops. Whatever the true explanation is, this run and Run SS15B indicate that the rate of mass transfer for the simultaneous extraction of acetone and n-butyl acetate was far more rapid than predicted for oscillating drops.

In Run SS7 isobutylene was used as the dispersed phase to extract a mixture of about 2000 ppm

Table 15. Interaction Among Solutes

Run #	V_w (ft/hr)	V_s (ft/hr)	Solute	E	Pe_w	% Removal	N_{ow} (expt'l)	N_{ow} (circul)	N_{ow} (oscill)
SS15A	23.3	52.3	Acetone	0.84	2.01	71.2	∞	0.42	1.36
			n-BuAc	224.		99.4	14.7	1.86	2.26
SS15B	23.3	26.9	Acetone	0.43	1.59	34.6	1.60	0.22	0.72
			n-BuAc	115.		93.2	5.44	1.00	1.19
SS7	21.6	68.0	MEK	4.65	2.09	77.7	2.51	1.46	2.95
			Crotonal.	4.63		77.0	2.43	1.46	2.95
SS12A	23.3	52.3	Acetone	0.84	2.02	36.5	0.69	0.42	1.37
			MEK	3.31		62.1	1.40	1.06	2.14
			Crotonal.	3.30		63.4	1.48	1.06	2.14
			n-BuAc	224.		72.0	1.68	1.87	2.27
SS12B	23.3	83.2	Acetone	1.33	2.44	47.0	0.94	0.66	2.15
			MEK	5.28		74.0	2.00	1.65	3.36
			Crotonal.	5.25		74.0	2.00	1.64	3.36
			n-BuAc	356.		80.5	2.25	2.86	3.57
SS16	23.3	52.3	Acetone	0.84	2.03	45.0	1.16	0.43	1.39
			MEK	3.31		68.2	1.81	1.06	2.12
			Crotonal.	3.30		67.7	1.77	1.06	2.12
			n-BuAc	224.		76.2	1.98	1.93	2.32

each of MEK (K_d = 2.49, Appendix E) and crotonaldehyde (K_d = 2.48, Appendix E). As shown in Table 15, the experimental values of N_{ow} for each solute were about 84% of what was predicted for oscillating drops. In Runs SS12 and SS16 all four of these solutes were present. The results show that all solutes gave experimental values of N_{ow} less than those predicted for oscillating drops. For the case of n-butyl acetate in Runs SS12A and SS12B, the experimental values of N_{ow} were even less than those predicted for circulating drops. Thus, when MEK and crotonaldehyde were added to the water stream containing acetone and n-butyl acetate, the factors which caused the rapid mass transfer during the extraction of acetone and n-butyl acetate alone seem to have been damped out.

In Run SS13 a prepared feed water containing about 2000 ppm each of acetone and n-butyl acetate plus about 300 ppm of benzene (measured K_d = 407.0) and about 4000 ppm of n-butanol (measured K_d = 0.76) was treated by isobutylene extraction. The results are compared with those for extraction of acetone and n-butyl acetate alone in Table 16. In Run SS13A as in Run SS15A the experimental removal efficiency for acetone was larger than what was predicted for perfect mass transfer, but when the solvent flow was reduced the experimental values of N_{ow} in both Runs SS13B and SS15B were more nearly in agreement with the prediction for oscillating drops. One possible explanation is that the value of Pe_w increased more rapidly with V_d than was predicted by equation (B6). For the purpose of comparison, the last column in Table 16 lists the experimental values of N_{ow}

Table 16. Interaction Among Solutes

Run #	V_w (ft/hr)	V_s (ft/hr)	Solute	E	Pe_w	% Removal	N_{ow} (expt with Pe_w finite)	N_{ow} (expt with $Pe_w = \infty$)	N_{ow} (predict oscill)
SS13A	23.3	52.3	Acetone	0.84	2.01	74.3	∞	4.17	1.37
			n-BuOH	1.01		77.9	∞	3.42	1.38
			n-BuAc	224.		99.7	17.5	5.70	2.27
			Benzene	543.		98.1	9.17	3.91	2.62
SS13B	23.3	26.9	Acetone	0.43	1.58	28.0	0.66	0.52	0.71
			n-BuOH	0.52		35.3	1.05	0.74	0.72
			n-BuAc	115.		90.7	4.47	2.35	1.18
			Benzene	279.		93.1	5.32	2.63	1.36
SS15A	23.3	52.3	Acetone	0.84	2.01	71.2	∞	3.31	1.36
			n-BuAc	224.		99.4	14.7	5.15	2.26
SS15B	23.3	26.9	Acetone	0.43	1.59	34.6	1.60	0.88	0.72
			n-BuAc	115.		93.2	5.44	2.66	1.19

calculated by assuming plug flow for both phases. Actual removal efficiencies of 61.0% and 66.7% for acetone and n-butanol, respectively, would have been necessary to give $N_{ow} = 5$ for these solutes. Considering all this information leads one to conclude that mass transfer was more rapid than predicted for oscillating drops in both Runs SS13 and SS15. Therefore, the addition of n-butanol and benzene did not damp out the high rate of mass transfer found for the extraction of acetone and n-butyl acetate without other components.

The results of these experiments do not lead to a clear understanding of this type of interaction between solutes, but they show that it can be important. The fact that this complicated interaction took place even for feed water prepared from pure chemicals indicates the need for mass transfer data using actual samples of industrial waste water.

In Run SS5 isobutylene was used to treat a waste water containing about 12,000 ppm each of phenol ($K_d = 0.70$, Appendix E) and vinyl acetate (measured $K_d = 52.0$). The measured removal efficiency of vinyl acetate (at $E = 69.2$) was 99.2% which corresponds to 13.2 for the experimental value of N_{ow} as compared to 2.53 predicted for oscillating drops. The measured removal efficiency for phenol (at $E = 0.93$) was 80.0%, which is not theoretically possible even for infinite N_{ow} and plug flow, if the value of K_d at infinite dilution applies. Using the estimated value of $Pe_w = 2.01$, the dispersion model predicts 64.2% removal for phenol at $N_{ow} = 5$. By a material balance the product isobutylene contained 8941 ppm vinyl acetate.

The results shown in Appendix F and by Won (1974) lead to the conclusion that the value of K_d^{mix} for phenol distributing between water and a mixture of isobutylene and n-butyl acetate is approximately given by the following for low concentrations of phenol:

$$K_d^{mix} = x_{BA}\, K_d^{BA} + (1 - x_{BA})\, K_d^{IB} \qquad (7)$$

where x_{BA} = wt. n-butyl acetate/(wt. n-butyl acetate + wt. isobutylene),

K_d^{BA} = distribution coefficient into pure n-butyl acetate,

K_d^{IB} = distribution coefficient into pure isobutylene.

The value of K_d^{mix} for phenol distributing between water and a mixture of isobutylene and vinyl acetate is about equal to that for a mixture of the same weight fraction of isobutylene and n-butyl acetate. Assuming $K_d^{BA} = K_d^{VA} = 57.0$, the value of K_d^{mix} for phenol distributing between water and an organic phase of the same composition as the product solvent is 1.20, which is high enough to explain the 80.0% removal of phenol. A calculation procedure that qualitatively explains this result is described in Appendix C.

Regeneration of Loaded Solvent.

At the completion of each of the experiments described so far, a sample of the regenerated solvent was analyzed using the Indalloy sampling method described in Chapter IV. Unfortunately the method of calibrating the gas chormatograph response was later found to be inaccurate. However, by assuming that the response factors for each component did not change with the quantity injected, a comparison of the chromatogram for the regenerated solvent with that for the loaded solvent provided an accurate estimate of the efficiency of solvent regeneration. The ratio of solute in the loaded solvent to that in the regenerated solvent ranged from 22 for ethylene dichloride to more than 200 for isoamyl alcohol. This result is a good indication of the relative ease of separating the solute from the volatile solvent, and it also serves to demonstrate the feasibility of solvent regeneration.

In Run SS8 a prepared feed water containing about 4000 ppm propionitrile (measured $K_d = 1.80$) and about 6000 ppm n-butanol (measured $K_d = 0.76$) was treated by isobutylene extraction. The removal efficiency for propionitrile varied from 91 to 96% and that for n-butanol varied from 79 to 88%; the results of an analysis of mass transfer are shown in Table 17. Once again the experimental value of N_{ow} was much larger than that predicted for oscillating drops. However, when the concentrations of solutes in the loaded solvent were compared to those in the regenerated solvent, we found that the concentration of propionitrile had only been reduced by 47% during solvent regeneration. A likely explanation is that propionitrile forms an azeotrope with isobutylene (estimated to contain 0.1% propionitrile from the estimate of the regenerated solvent composition) which prohibits more complete regeneration of the solvent. The concentration of n-butanol in the

Table 17. Extraction of n-Butanol and Propionitrile

Run #	V_w (ft/hr)	V_s (ft/hr)	Solute	E	Pe_w	% Removal	N_{ow} (experimental)	N_{ow} (oscillating)
SS8A	15.4	36.1	n-BuOH	1.06	1.15	78.5	∞*	1.44
			Pr-CN	2.51		90.7	16.8	2.10
SS8B	15.4	68.0	n-BuOH	1.99	1.48	88.1	12.8	2.69
			Pr-CN	4.72		96.1	14.1	3.92

* Dispersion model predicts for $E = 1.06$, $Pe_w = 1.15$, and $N_{ow} = 12$, % Removal = 67.8

loaded solvent was reduced by 97% in the same regeneration.

Of all the solutes studied, only propionitrile showed a tendency to form an azeotrope. Since the most important other nitrile pollutants (acetonitrile and acrylonitrile) are more volatile than propionitrile, it is likely that all these nitriles will form azeotropes with isobutylene. Thus, volatile solvent extraction of the lower-molecular-weight nitriles is not feasible in a process using isobutylene as solvent and distillation for regeneration.

Industrial Waste Waters.

The initial runs made to establish and improve the experimental apparatus and techniques were conducted in preparation for treating samples of lube oil refining waste water. For this reason in Runs SS1, SS2 and SS4 a prepared feed water containing about 2% phenol and 0.1 to 1.0% o-cresol was treated by isobutylene extraction. In these runs the phenol removal efficiency varied from 76 to 88%, and the o-cresol removal efficiency varied from 95 to 97%. The results of an analysis of mass transfer rates are shown in Table 18. The experimental values of N_{ow} were much larger than N_{ow} predicted for oscillating drops in all cases; two results showed that the measured phenol removal efficiency should be impossible even with infinite N_{ow}. The results indicate that interfacial turbulence was probably occurring during the extraction of these relatively concentrated water streams.

In Runs SS3 and SS6 samples of lube oil refining waste water were treated by isobutylene

Table 18. Extraction of Phenol and o-Cresol

Run #	V_w (ft/hr)	V_s (ft/hr)	Solute	E	Pe_w	% Removal	N_{ow} (expt'l)	N_{ow} (oscill)
SS1	19.4	82.4	Phenol	1.76	2.03	79.1	4.76	2.52
			o-Cresol	12.1		95.1	6.66	4.02
SS2	22.2	71.6	Phenol	1.34	2.18	88.2	∞*	1.89
			o-Cresol	9.21		96.6	8.42	3.00
SS4A	22.5	71.6	Phenol	1.32	2.23	85.6	(37.5)*	1.90
			o-Cresol	9.05		96.1	7.56	3.03
SS4B	22.5	52.5	Phenol	0.97	1.96	76.0	∞*	1.40
			o-Cresol	6.63		95.3	8.11	2.23

* Dispersion model predicts for the listed values of E and Pe_w and $N_{ow} = 5$ for Phenol Run SS2, % Removal = 74.8; Run SS4A, % Removal = 74.7; and Run SS4B, % Removal = 65.3

extraction. The phenol and o-cresol removal efficiencies in Run SS3 were 40% and 67%, respectively. The substantial reduction in removal efficiency as compared to the prepared waste waters was determined to be due to two factors -- (1) the feed isobutylene had not been properly regenerated and contained an unknown amount of phenol and o-cresol from a previous run, and (2) the pH of the waste water was about 9, which has been shown by Beychok (1967) to lead to a reduction in K_d for phenolic compounds. These results led to the installation of the refluxed distillation column on the miniplant evaporator and to the practice of acidifying this waste water to a pH of about 4 prior to phenol extraction. The isobutylene used in the extraction of prepared waste waters had been either used fresh or regenerated by back extracting the phenol and o-cresol into a dilute caustic solution. Run SS3 also led to the realization that solutes other than phenol and o-cresol were present at lower concentrations; these were later identified as acetone, MEK, and benzene.

In Run SS6 another sample of lube oil refining waste water was treated by isobutylene extraction. The results of an analysis of mass transfer rates are shown in Table 19; the last column headed "Q" is the ratio of experimental N_{ow} to N_{ow} predicted for oscillating drops. This is the first case where Q was consistently less than 1 for some solutes (acetone and benzene in Run SS6B) and greater than 1 for the other solutes. The values of Q for phenol and o-cresol, the major pollutants, were fortunately the largest. It is interesting to note that Q was smallest for the solute with the lowest and

Table 19. Extraction of Lube Oil Refining Waste

Run #	V_w (ft/hr)	V_s (ft/hr)	Solute	E	Pe_w	% Removal	N_{ow} (expt'l)	N_{ow} (oscill)	Q
SS6A	21.6	92.2	Acetone	1.60	2.35	56.8	1.37	2.56	0.53
			Phenol	1.77		80.2	4.74	2.48	1.91
			MEK	6.31		94.8	7.03	3.88	1.81
			o-Cresol	12.2		97.5	8.98	3.96	2.27
			Benzene	1032.		95.9	5.99	4.90	1.22
SS6B	21.6	52.0	Acetone	0.90	1.87	40.5	0.85	1.47	0.58
			Phenol	1.00		58.9	2.51	1.43	1.76
			MEK	3.56		76.3	2.62	2.24	1.17
			o-Cresol	6.86		83.9	3.31	2.28	1.45
			Benzene	582.		79.4	2.27	2.82	0.81

the solute with the highest value of K_d: this tends to rule out a correlation between Q and E. Q generally decreased as V_d decreased at a constant value of V_c.

In Run SS14 cresylic acid recovery waste water was treated by isobutylene extraction. The removal efficiencies varied from 72% for phenol to almost 96% for xylenols. The results of analyzing the mass transfer aspects of this run are shown in Table 20. The values of Q were again greater than 1 for all solutes.

In all three runs where isobutylene was used to treat industrial waste water, the feed water contained suspended, fine particles, but in no case was there a substantial flotation effect. During the treatment of lube oil refining waste water there was a slight accumulation of suspended material at the main interface. This accumulation did not appear to be the fine particles, but rather a sticky material that caused some problems of delayed droplet coalescence.

The measurement of Chemical Oxygen Demand (COD) for the feed and treated industrial waste waters can yield useful data about the fate of dissolved and suspended organic pollutants which are not observed with the gas chromatograph. In Run SS6 the COD's of the feed and product lube oil refining waste water streams were not measured. However, subsequent experiments in which this waste water was treated (see Section VIII) show that COD calculated from the amounts of identified pollutants agrees well with the measured COD. In Run SS14 the measured COD's of the feed and treated cresylic acid recovery

Table 20. Extraction of Cresylic Acid Recovery Waste

Run #	V_w (ft/hr)	V_s (ft/hr)	Solute	E	Pe_w	% Removal	N_{ow} (expt'l)	N_{ow} (oscill)	Q
SS14	20.1	60.6	Phenol	1.25	1.85	71.8	5.01	1.78	2.82
			m, p-Cresol	4.82*		91.3	6.12	2.60	2.35
			o-Cresol	8.57		89.8	4.60	2.83	1.62
			Xylenols	12.5*		95.6	7.40	2.79	2.65

* E for m, p-Cresol calculated assuming $K_d = K_d$ (for m-Cresol) = 2.7, and E for Xylenols calculated assuming $K_d = K_d$ (for 3, 5-Xylenol) = 7.0 (Appendix E).

waste water were 4050 ppm and 1070 ppm (74% reduction). These values can be compared to the COD's of the feed and treated streams as calculated from the identified phenolic compounds which were 3840 ppm and 560 ppm (84% reduction). The nearly constant difference between measured and calculated values indicates that the components which account for this difference were not well extracted. The fine solids which were obviously not well removed probably contributed to the difference between measured and calculated COD's.

Overall Process Feasibility.

In the experiments conducted in the spray column extractor, a wide variety of organic solutes was extracted by isobutylene, and in no case was there an irreversible reaction between solvent and solute. The only case of any solvent degradation occurred in an auxilliary experiment where isobutylene hydration was noted in a strongly acidic aqueous solution.

The removal efficiency for most cases indicated a mass transfer rate substantially larger than that predicted for oscillating drops. However, an unexplained damping out of the factors which caused this high rate was noted for all combinations of solutes containing MEK and crotonaldehyde. Even with the two samples of industrial waste water, there was no indication of an interfacial effect which would inhibit mass transfer. The use of solvent extraction did not lead to an appreciable flotation of suspended solids.

The short, refluxed distillation column provided a very effective means for solvent regeneration. Only in the case of propionitrile was solvent regeneration not feasible, probably because of an azeotrope.

SECTION VIII

RDC EXTRACTOR - EXPERIMENTAL RESULTS

During the second portion of the experimental program, several prepared aqueous solutions and industrial waste waters were treated by solvent extraction in the RDC as described in Section VI. Experiments included runs using volatile solvents, less-volatile polar solvents, and mixtures of volatile and polar solvents. In these experiments the solvent was always the dispersed phase, and the solvent-to-water flow ratio (F_s/F_w) was set at much lower values than with the spray column. F_s/F_w was varied over the range from 0.1 to 0.3 in order to demonstrate solvent extraction under conditions which would be most likely to lead to favorable process economics.

In addition to the choices of solvent and the value of F_s/F_w, the independent variables which could be varied on the RDC included the water flow rate, the disc rotational speed, the disc diameter, the stator hole diameter, and the compartment height. The principal measured responses were the solvent hold-up, the concentrations of each solute in the product water and in the water within the RDC just below the main interface, and in most runs the concentration of each solute in the loaded solvent.

The temperature was measured but not controlled. An approximate measurement was made of the maximum stable solvent droplet diameter by holding a scale against the glass column. From the "whole run" material balance (see Section VI), it was possible to estimate the effectiveness of solvent regeneration in runs using a volatile solvent. The batch distillation of polar solvent also gave a qualitative measure of the ease of solvent regeneration.

The method by which the independent variables were chosen in each experiment involved some trial and error. Treybal (1963) cites the following ranges for the ratio of column diameter to rotating disc diameter, D/d_i, and the ratio of column diameter to compartment height, D/H_c, as preferred proportions for commercial RDC extractors:

$D/d_i = 1.5$ to 3

$D/H_c = 2$ to 8

The dimensions of RDC extractors in the studies reviewed by Ingham (1971) fell into these ranges, and the ratio of column diameter to stator hole diameter, D/d_s, in these studies fell into the following range:

$D/d_s = 1.2$ to 1.6

The value of D was chosen to be as large as possible and still be small enough so that the pressure within the column could be contained by industrial glass pipe For operation with isobutane as solvent this resulted in D = 3 inches. For the initial tests based on the above ranges of ratios, the other dimensions were chosen as follows:

$d_i = 1.50$ inch

d_s = 2.25 inch

H_c = 1.00 inch

In the studies reviewed by Ingham (1971) where water was the continuous phase, the highest value of V_c in each study ranged from 15 to 50 ft/hr. Since for most industrial waste water samples we could obtain only 5- to 10-gallon quantities we chose to operate at the low end of this range with a maximum V_c of 15 ft/hr and a minimum V_c of 6 ft/hr.

Once the column dimensions, V_c, and F_s/F_w had been chosen, the remaining independent variable was the disc rotational speed, N. Correlations such as that of Logsdail, et al. (1957) can be used to estimate the value of N at the flooding point, but as discussed in Section V flooding in an RDC does not suddenly occur as N is increased. Also, the value of the interfacial tension is required in the correlation, and the interfacial tension for a waste water can be substantially below the known value for the solvent-water binary mixture.

For these reasons the operating value of N was chosen by experimental observation as follows. With the waste water and solvent flows established, N was slowly increased. At low rotational speeds, the solvent droplets were large and good contact between water and solvent was not obtained. As N increased, contact between phases improved until small solvent droplets could be seen in the quiescent zone below the bottom disc. When a value of N was determined which resulted in the entrainment of what appeared to be about 1% solvent in the water phase, N was decreased by about 10% to establish its operating value. This procedure resulted in operation at a practical set of conditions which should be reasonably close to what would be used in a commercial extractor.

In this chapter we first describe an experiment which was designed to determine how useful existing correlations for RDC extractors would be in predicting the observed performance with respect to hydrodynamics, axial mixing, and mass transfer rates. The correlations are shown to depend strongly on the choice of the constant G_{18} (Eq. B12). The remaining experiments were grouped according to the type of industrial waste water being studied. The lube oil refining waste water was treated using dual solvent extraction with n-butyl acetate and isobutylene. Both process arrangements of dual solvent extraction are demonstrated to result in effective removal of phenol and o-cresol and moderate removal of the other solutes. Experiments in which the ethylene quench water was treated by volatile solvent extraction show effective removal of aromatic hydrocarbons; isobutane was a better solvent than isobutylene for removal of dispersed organics. Treatment of the oxychlorination waste water using 2-ethyl hexanol is shown to be complicated by a simultaneous chemical reaction between the solvent and the principal solute, chloral hydrate. The experimental results for all runs conducted in the RDC are listed in Appendix H; run numbers start with the prefix RS to signify Rotating disc extractor with Solvent dispersed.

Test Run To Check RDC Correlations.

One experiment was conducted in which n-butyl acetate was dispersed with $F_s/F_w = 0.1$ into a water stream which contained methyl acetate (measured $K_d = 3.64$), ethyl acetate (measured $K_d = 11.2$) isopropyl acetate (measured $K_d = 34.1$), and o-cresol ($K_d = 206$, Appendix F). This prepared water was not made up to simulate any particluar waste stream, but rather the solutes and their concentrations in the feed water were chosen to satisfy the following criteria which were established to obtain the maximum amount of information about the rates of mass transfer:

1. Solutes should cover a range of E from about 0.3 to greater than 10,
2. Solutes and the solvent must be separable using a gas chromatograph so that their concentrations can be simultaneously determined,
3. The concentrations of all solutes must be high enough in the product water so that their concentrations can be accurately determined,
4. The concentrations of all solutes must be low enough in the feed water to be completely miscible,
5. The concentrations of all solutes should be as low as possible so that each value of K_d can be estimated at its infinite dilution value, and
6. Solutes should ideally be separable from the solvent by distillation so that the solvent can be regenerated.

Since n-butyl acetate was a solvent of particular interest in this study, it was chosen for this test run. The choice of the lower molecular weight acetates provided solutes with K_d from 3.6 to 34 while satisfying requirements 2 through 6. K_d was found to vary only a little with solute concentration for these systems. Amyl acetate (measured K_d = 700) could not be used as a solute showing a very high value of K_d because its solubility was too low to satisfy both requirements 3 and 4. Cresol was chosen since it had K_d = 206 and still had a water solubility of greater than 2%. However, the presence of about 5% o-cresol in the loaded solvent may have affected K_d at the upper end of the column, thus violating requirement 5.

The results of this test run (Run RS13) are shown in Table 21. The percentage of each solute removed varied from 20.3% for methyl acetate (E=0.41) to 95.5% for o-cresol (E=23.0). The n-butyl acetate in the product water includes 4 ppm (of the 6600 ppm) due to entrained n-butyl acetate phase. This estimate was determined by collecting the n-butyl acetate phase which appeared on the surface of the treated water after it had separated in the receiving tank on sitting for about five days.

At the column temperature of 21.6°C, the physical properties of the pure solvent and of pure water along with the solute diffusivities as estimated by the method of Scheibel (1954) are listed in Table 22. The solvent density and viscosity are from Toropov (1956). The interfacial tension at 20°C was taken from Logsdail, et al (1957), and the correlation of Donahue and Bartell (1952) was used to correct for the slight difference in temperature.

Table 21. Results from RDC Test Run RS13

Water flow rate = 4.79 gal/hr

Solvent flow rate = 0.606 gal/hr

Rotating disc diameter = 1.50 inch

Stator hole diameter = 2.25 inch

Rotational speed = 800 RPM

Analytical results (concentrations in ppm):

	Methyl Acetate	Ethyl Acetate	i-Propyl Acetate	o-Cresol
Feed Water	227.	270.	676.	5622.
Product Water	181.	81.6	85.3	255.
Percent Removal	20.3	69.8	87.4	95.5
Water in Column	235.	248.	509.	3349.
Loaded Solvent	497.	1882.	5944.	51120.

n-Butyl acetate in product water = 6600 ppm.

Measured solvent hold-up = 0.0428

Measured column temperature = 21.6°C

Estimated maximum drop diameter = 0.05 inch

Table 22. Physical Properties for Run RS13

Water-phase density = 0.9979 gm/cc

Water-phase viscosity = 0.9642 cp

n-Butyl Acetate density = 0.8792 gm/cc

n-Butyl Acetate viscosity = 0.708 cp

Interfacial tension = 13.9 dyne/cm

Solute diffusivities ($10^5 \times ft^2/hr$) in water (D_c) and in n-butyl acetate (D_d):

Solute	D_c	D_d
Methyl Acetate	3.93	6.45
Ethyl Acetate	3.40	5.97
i-Propyl Acetate	3.04	5.60
o-Cresol	3.02	5.57

From the information in Tables 21 and 22 the steady state material balance around the extraction column was calculated. It showed that the total quantity of each solute present in the product water and in the loaded solvent exceeded the measured quantity of solute in the feed water by 2.7% for methyl acetate, by 4.1% for ethyl acetate, by 6.0% for isopropyl acetate, and by 1.0% for o-cresol. The closures for these solutes in this run were slightly worse than for a typical run with a polar solvent and were somewhat better than for a typical run using a volatile solvent.

The inlet flows to the column were $F_s = 4.45$ lb/hr and $F_w = 39.9$ lb/hr ($F_s/F_w = 0.111$). Based on the concentration of n-butyl acetate in the purified water, the quantity of solvent decreased by about 6% as it passed through the column. However, the total solute extracted into the solvent almost exactly balanced the dissolved solvent so that the total solvent-phase mass flow rate was nearly constant. For this reason the analysis of this run using the dispersion model was made in terms of total flows and weight fractions rather than solvent flows and weight ratios.

The experimentally measured fractional solvent hold-up is an average value for the portion of the column between the bottom disc and the main interface. Visual inspection showed that there was a variation in hold-up along the column. The drops were not broken up to an equilibrium drop size distribution at the bottom disc, but rather there was an obvious increase in hold-up as the drops were broken up between the bottom disc and about the fifth disc from the bottom. Between the fifth disc and the twelfth disc the hold-up appeared to be approximately constant. The hold-up increased substantially between the twelfth disc and the mid-column bearing because of the decrease in free flow area offered by the bearing (about 24% free area compared to $C_R = 0.52$). For several discs above the bearing the hold-up increased until it reached a value about like that between the fifth and twelfth discs from the bottom; then it remained approximately constant up to the main interface. Therefore, the measured hold-up is probably not equal to that of the equilibrium drop size distribution.

This variation in hold-up along the column made the quantitative analysis of the hydrodynamics very difficult. In the procedure of Strand, et al. (1962) as described in Appendix B, the one adjustable parameter, G_{18}, is usually estimated from the hold-up. For the n-butyl acetate-water system Strand, et al. (1962) estimated $G_{18} = 0.4$ from hold-up measurements. For several systems with water as the continuous phase, but not including n-butyl acetate-water, Olney (1964) found the ratio of Sauter mean drop diameter to maximum stable drop diameter was about 0.37, which when combined with an estimated maximum stable drop diameter of 0.05 inch gives $d_p = 0.02$ inch. In Table 23 values of hold-up, $\emptyset$, Sauter mean drop diameter, d_p, interfacial area per unit volume, a, characteristic velocity according to the method of Strand, et al. (1962), V_k, and the two Peclet numbers, Pe_c and

Pe_d, are listed for three values of G_{18}. G_{18} = 0.0477 results from the experimentally determined hold-up. G_{18} = 0.2 gives a Sauter mean drop diameter of about that estimated from the measured maximum stable drop diameter. G_{18} = 0.4 corresponds to the estimate of Strand, et al. (1962).

The data in Table 23 serve to show how sensitive the predictions of the hydrodynamic characteristics of an RDC are to the choice of G_{18}, and how difficult it is to choose a value of G_{18} from experimental data on a single experiment. The correlation of Logsdail, et al. (1957) predicts V_k = 128 ft/hr for this system; this fact along with the measured drop size makes the value of G_{18} = 0.2 appear reasonable. The importance of the choice of G_{18} on the prediction of N_{ow} is illustrated by the variation of a with G_{18}, if one realizes that N_{ow} is proportional to a.

Table 24 shows that the variation in G_{18} has little effect on the evaluation of the experimental N_{ow} for each component. The experimental values of N_{ow} were calculated from the measured removal efficiency, the values of E, and the two Peclet numbers. Of the variables affecting N_{ow}, only Pe_c and Pe_d vary with G_{18}, and the variation is not large enough to affect the experimental N_{ow} substantially. The values of E and % removal based on the analyses of feed and product water are included in Table 24.

The experimental data for N_{ow} calculated assuming G_{18} = 0.2 are plotted as $1/N_{ow}$ vs. 1/E

Table 23. Effect of G_{18} on Prediction of Hydrodynamic Characteristics of RDC

G_{18}	ϕ	d_p (inch)	V_K (ft/hr)	a (ft^2/ft^3)	Pe_c	Pe_d
0.0477	0.0428	0.005	55	606	8.41	13.0
0.20	0.0124	0.021	149	42	8.19	29.0
0.40	0.0073	0.043	242	12	8.15	36.6

Table 24. Effect of G_{18} on the Experimental Estimates of N_{ow}

	Methyl Acetate	Ethyl Acetate	i-Propyl Acetate	o-Cresol
G_{18}	N_{ow}	N_{ow}	N_{ow}	N_{ow}
0.0477	0.35	2.7	3.4	4.4
0.20	0.34	2.5	3.2	4.3
0.40	0.34	2.5	3.2	4.3
E	0.41	1.25	3.80	23.0
% Removal	20.3	69.8	87.4	95.5

in Figure 27. The points for ethyl acetate, isopropyl acetate, and o-cresol fall within experimental variation on a straight line, but the point for methyl acetate is much above the line. The removal efficiency for methyl acetate would have to be 36% rather than 20% for that point to have fallen on the line; this large a variation is much more than what can be explained by experimental variation. This observed low experimental value of N_{ow} for a component with E much less than 1 has been observed in several other experiments in the RDC and may be the result of the failure of the dispersion model to predict the concentration changes for such solutes. Concentration profiles, which were not measured in the present experiments, would be required to verify this possibility.

Although concentration profiles over the entire length of the column were not measured, after reaching steady state one sample was taken of the continuous aqueous phase from a point just below the main interface. In terms of the dimensionless position variable, Z, defined as the distance below the main interface divided by the total length from the main interface to the bottom disc, $Z = 0.034$ specifies the position from which the sample was taken. The measured solute concentrations were included in Table 21; the solute concentrations predicted by the dispersion model with $G_{18} = 0.2$ at the point $Z = 0.034$ are compared to the measured concentrations in Table 25.

The straight line through the data points for the three solutes having $E > 1$ results in $N_w = 4.2$

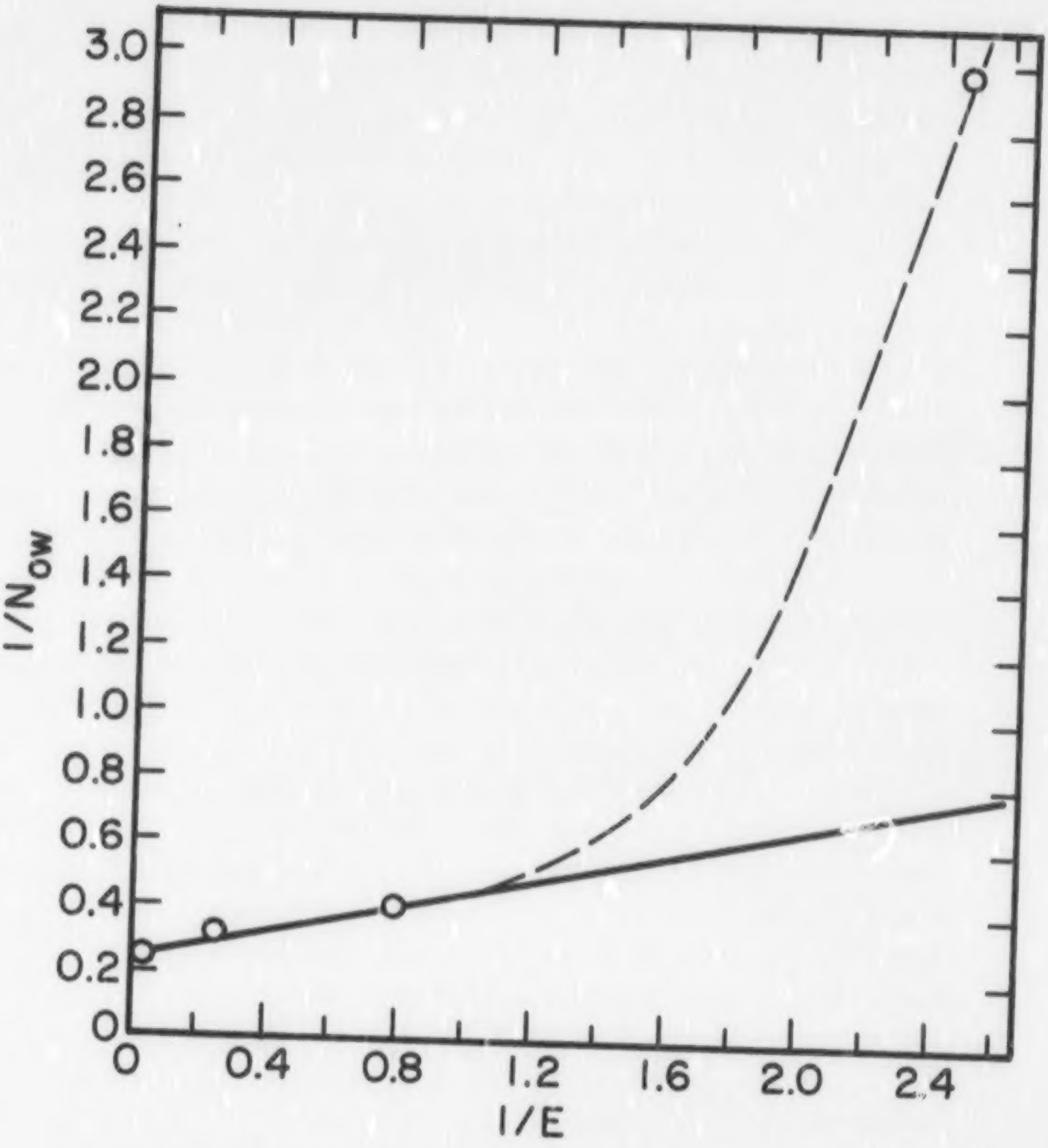


Figure 27. Experimental Data for Run RS13

Table 25. Comparison of Predicted and Experimental Solute Concentrations for $Z = 0.034$ and $G_{18} = 0.2$

Solute	Experimental Concentration, ppm	Predicted Concentration, ppm	% Difference
Methyl Acetate	235	221	-6.0
Ethyl Acetate	248	237	-4.4
i-Propyl Acetate	509	515	1.2
o-Cresol	3349	3682	9.9

and $N_s = 5.0$ for the individual-phase numbers of transfer units. In Tables 26 and 27 the values of the N_w and N_s predicted by the various models for mass transfer discussed in Chapter III are shown as a function of G_{18}. If G_{18} is assumed to be approximately 0.2, then the model for turbulent drops gives the best estimate for N_w, and both the models for circulating drops and for stagnant drops give a value of N_s that is much too large. The uncertainty in G_{18} prohibits one from making a clear choice between models from these limited data.

The results of this single experiment have been presented in detail to illustrate the successes and failures of the presently available methods for modeling an RDC. The ability to estimate the individual-phase resistances to mass transfer experimentally, which is possible by the collection of mass transfer data on the simultaneous extraction of several solutes, provides a severe test to the present model. Clearly more experimental work is needed to improve our ability to correlate data from an RDC.

Experiments on Lube Oil Refining Waste Water

This waste water was the most thoroughly studied sample of all the industrial waste water samples tested in the RDC. The two types of dual solvent processes (Section IV) were simulated by separate extractions, first with pure n-butyl acetate or with a mixture of n-butyl acetate and isobutylene. Then the resulting purified water from the first extraction was treated with pure isobutylene. The

Table 26. Effect of G_{18} on the Prediction of N_w for the RDC

	Methyl Acetate	Ethyl Acetate	i-Propyl Acetate	o-Cresol
G_{18}	N_w	N_w	N_w	N_w
	Stagnant Drops - Equation (B22)			
0.0477	5.9	5.9	5.9	5.9
0.20	1.1	1.1	1.1	1.1
0.40	0.55	0.55	0.55	0.55
	Circulating Drops - Equation (B24)			
0.0477	280.	260.	250.	250.
0.20	16.	15.	14.	14.
0.40	4.2	3.9	3.7	3.7
	Turbulent Drops - Equation (B26)			
0.0477	34.	31.	29.	29.
0.20	2.4	2.1	2.0	2.0
0.40	0.69	0.63	0.58	0.58

Table 27. Effect of G_{18} on the Prediction of N_s for the RDC

G_{18}	Methyl Acetate N_s	Ethyl Acetate N_s	i-Propyl Acetate N_s	o-Cresol N_s
Stagnent Drops - Equation (B23)				
0.0477	890	830	780	770
0.2	15	14	13	13
0.4	2.2	2.0	1.9	1.9
Circulating Drops - Equation (B25)				
0.0477	990.	930.	880.	870.
0.2	34.	33.	32.	32.
0.4	12.	11.	11.	11.

initial tests of the RDC (Runs RS1A, RS1B, and RS2) are also discussed in this section since the prepared feed waters resemble the lube oil refining waste water. The analysis of mass transfer characteristics for all runs dealing with this waste water are discussed together at the end of this section.

In Run RS2 n-butyl acetate was used to treat a feed water prepared to contain methyl ethyl ketone (MEK, measured $K_d = 4.56$), diethyl ketone (DEK, measured $K_d = 16.2$) and phenol ($K_d = 57.0$, Appendix F) while operating at a low flow ratio ($F_s/F_w = 0.120$). The settings of independent variables and the results of the extraction are shown in Table 28. This experiment was conducted prior to the installation of the level gauge used to measure solvent hold-up and prior to the installation of the sampling port for removing samples from within the column. Also, the solvent feed was not directed through the annular space between the rotating shaft and the bottom stationary tube, but it was added through a tube which extended to about 2 inches below the bottom disc.

The material balance for this run showed a loss of 12.5% of the inlet MEK, a loss of 5.7% of the inlet DEK, and a gain of 2.5% of the inlet phenol. The concentration of n-butyl acetate in the product water was also unexpectedly low compared to its solubility. These results led to several tests which showed that the paper seals in the sample vials could absorb a considerable amount of the volatile organic solutes from the aqueous samples (see discussion in Section VI). Since the sample of feed water was taken into a glass stoppered bottle but the product water samples

Table 28. Results from Run RS2

Water flow rate = 5.16 gal/hr

Solvent flow rate = 0.701 gal/hr

Rotating disc diameter = 1.50 inch

Stator hole diameter = 2.25 inch

Rotational speed = 617 RPM

Analytical results (concentrations in ppm):

	MEK	DEK	Phenol
Feed water	2213.	4314.	6143.
Product water	1135.	1238.	1228.
Loaded solvent	6508.	22860.	40910.
Percent removal	36.2	65.6	82.5

n-Butyl acetate in product water = 4986 ppm.

E	0.55	1.94	6.82
N_{ow}	0.88	1.6	2.3

Measured column temperature = 22.0 °C

G_{18} assumed to be 0.2 giving $Pe_w = 8.53$

and $Pe_s = 28.1$

were taken into the 5 cc sample vials, absorption by the seal would account for the MEK and DEK losses and for the low concentration of n-butyl acetate.

Due to the errors in the product water analyses, the removal efficiencies listed in Table 28 were calculated from the feed water analysis and the loaded solvent analysis by assuming that the material balance was exact. Using the inlet solvent and water flows, the values of E were determined for each solute. Assuming $G_{18} = 0.2$ as found to be reasonable for Run RS13 when n-butyl acetate was used as solvent, the values of Pe_w and Pe_s were estimated. This allowed the values of N_{ow} to be calculated for each solute and allowed a plot of $1/N_{ow}$ vs. $1/E$ to be made. The three points fell almost exactly on a straight line resulting in $N_w = 2.5$ and $N_s = 2.4$ as experimental estimates. The values of N_w and N_s were about half as large as found in Run RS13; this is probably due to using fewer discs, having poorer solvent dispersion, and using a lower rotational speed in Run RS2 than in RS13.

In Runs RS1A and RS1B isobutylene was used to treat a prepared feed water which contained MEK ($K_d = 2.49$), DEK ($K_d = 13.4$), and n-butyl acetate ($K_d = 168$) (see Appendix E) while operating at two settings of the solvent flow rate ($F_s/F_w = 0.354$ and 0.117). The setting of the independent variables and the results of the extraction are shown in Table 29. The RDC was set up exactly as in Run RS2 just previously described. As with the spray column experiments, the material balance could not be checked because the

Table 29. Results from Runs RS1A and RS1B

Water flow rate = 2.28 gal/hr
Rotating disc diameter = 1.50 inch
Stator hole diameter = 2.25 inch
Rotational speed = 1430 RPM
Measured column temperature = 22.0 °C

Run RS1A Solvent flow rate = 1.36 gal/hr

Analytical results (concentrations in ppm):

Feed water	2109.	4297.	4393.
Product water	639.	183.	77.3
Percent removal	69.7	95.7	98.2
E	0.88	4.74	59.4

Run RS1B: Solvent flow rate = 0.450 gal/hr

Analytical results (in ppm):

Feed water	2109.	4297.	4393.
Product water	1340.	888.	288.
Percent removal	36.5	79.3	93.4
E	0.29	1.57	19.7

volatile solvent sampling procedure had not been perfected.

It is difficult to interpret this experiment using the dispersion model. Subsequent experiments described below which use isobutylene as a solvent indicate that a reasonable range of values for G_{18} is from 0.15 to 0.30. Values of G_{18} in this range lead to $Pe_w = 1.9$ which is characteristic of extensive axial mixing in the continuous phase. Using this value for Pe_w and the corresponding prediction for Pe_s between 24 and 29, the dispersion model predicts that the observed removal efficiencies for MEK in Runs RS1A and RS1B are not possible even for infinite N_{ow}. The model also predicts large values of N_{ow} for DEK (11 for RS1A and 7 for RS2A) and for n-butyl acetate (10 for RS1A and 6 for RS2A). These values are not only larger than expected, but they also decrease with increasing E which violates the additivity of resistances concept. No explanation for these observations is available.

Although the quantitative explanation for these results is unknown, visual observation agreed with predicted values of Pe_w as considerable mixing of the continuous phase was apparent. This observation led to the fabrication of a second set of discs and stator plates having a disc diameter of 1.75 inch (1.50 inch for initial discs) and a stator hole diameter of 2.00 inch (2.25 inch for initial stator holes). For all subsequent tests using volatile solvents, this second set of discs and stator plates was used; this practice led to much larger values of Pe_w and better removal efficiencies. These new dimensions are also within typical ranges of commercial RDC extractors.

In Runs RS3 and RS4 a waste water which was prepared to simulate the lube oil waste was extracted first with n-butyl acetate (RS3) and then with isobutylene (RS4). The feed water to Run RS3 which contained acetone (measured K_d = 1.05), MEK (measured K_d = 4.56), phenol (K_d = 57.0, Appendix F), benzene (measured K_d = 61.5), and o-cresol (K_d = 206, Appendix F) was treated at a low flow ratio of n-butyl acetate to water (F_s/F_w = 0.097). The settings of independent variables and the results of the extraction are shown in Table 30. The steady state material balance closed within less than 6% for each of the five components. The total solvent-phase flow rate increased by almost 9% because of the addition of solutes, while the flow of n-butyl acetate in the solvent decreased by about 6% due to solubility losses in the water. Therefore, the analysis was calculated on a solute-free flow basis using the inlet solvent flow rate.

The analysis of this run showed the same conflict in choosing the best value of G_{18} as was encountered in Test Run RS13. Assuming as before that G_{18} = 0.2, the method of Strand, et al. (1962) was used to estimate Pe_w and Pe_s from which the values of N_{ow} listed in Table 31 were calculated using the experimental removal efficiencies. The ratio of solute-free flows was 0.0992 lb. solvent/lb. water from which the values of E were determined. The percent removal values listed in Table 31 were

Table 30. Results from Run RS3

Water flow rate = 5.65 gal/hr

Solvent flow rate = 0.626 gal/hr

Rotating disc diameter = 1.50 inch

Stator hole diameter = 2.25 inch

Rotational Speed = 805 RPM

Analytical results (concentrations in ppm):

	Acetone	MEK	Phenol	Benzene	o-Cresol
Feed water	38.0	217.	13300.	169.	2107.
Product water	34.3	126.	308.	30.5	25.4
Percent removal	9.7	41.9	97.7	82.0	98.8
Water in column	32.5	181.	6820.	19.0	649.
Loaded solvent	44.9	974.	115000.	1292.	20300.

n-Butyl acetate in product water = 6110 ppm.

Measured solvent hold-up = 0.0630

Measured column temperature = 22.0°C

Estimated maximum drop diameter = 0.05 inch

Table 31. Experimental Estimates of N_{ow} for Run RS3

	Acetone	MEK	Phenol	Benzene	o-Cresol
E	0.10	0.45	5.65	6.10	20.4
% Removal	9.7	41.9	97.7	82.0	98.8
N_{ow}	0.4	2.5	6.6	2.2	6.7

G_{18} assumed to be 0.2; $Pe_w = 9.55$
and $Pe_s = 29.2$

calculated from the solute-to-water weight ratios in the aqueous phase. Using G_{18} = 0.2 led to a calculated solvent hold-up of 0.0126 which can be compared to $\emptyset$ = 0.0630, the measured value.

When the data from RS3 were plotted as $1/N_{ow}$ vs 1/E, the points for phenol and o-cresol essentially coincided. If a straight line were drawn through this point and through the point for MEK, N_w = 7.3 and N_s = 8.4 were determined as the individual-phase numbers of transfer units. The point for acetone fell above the line through the points for phenol, o-cresol, and MEK much as the point for methyl acetate did in Run RS13 (Figure 27), but in Run RS3 the removal efficiency for acetone would only need to be changed from 9.7% to 10.3% to make the point for acetone fall on the line. This difference is within experimental uncertainty. The point for benzene which also fell above the straight line cannot be explained as experimental uncertainty. A low removal efficiency for benzene when benzene was present with this combination of solutes has been observed in several experimental runs including SS6 in the spray column. Chromatographic analysis of the feed solvent showed that it was free of benzene.

In Run RS4 the collected water which had been treated by n-butyl acetate extraction in RS3 was treated with isobutylene at a low solvent-to-water flow ratio (F_s/F_w = 0.100). The major solute was n-butyl acetate (K_d = 168, Appendix E) with smaller amounts of acetone (K_d = 0.63, Appendix E), phenol (K_d = 0.7, Appendix E), MEK (K_d = 2.49, Appendix E), o-cresol (K_d = 4.8, Appendix E), and benzene (measured K_d = 407). The settings of independent variables and the results of the treatment are shown in Table 32. The dramatic improvement in column performance due to changing to larger discs and to stators with smaller holes is evident by comparing n-butyl acetate removal efficiency in RS1B (93.4%) with n-butyl acetate removal efficiency in RS4 (99.8%). The material balance closures for each solute were within 15%; the main error was still believed to be in the analyses of organic-phase samples containing the volatile solvent.

Using the method of Strand, et al. (1962), G_{18} = 0.337 was estimated from the measured solvent hold-up. The variation of solvent hold-up along the length of the RDC appeared to be much less pronounced in this run than in runs using n-butyl acetate as solvent. With the larger disc and smaller stator holes the restriction of free flow area due to the mid-column bearing was less severe (about 24% free area compared to C_R = 0.25); this was probably the major reason for a more uniform hold-up. The value of G_{18} calculated from the average hold-up resulted in a calculated average droplet size which agreed with visual estimation.

Values of N_{ow} for each solute were estimated using G_{18} = 0.337 to estimate Pe_w = 4.92 and Pe_s = 32.0, using K_d for pure isobutylene as solvent, and using experimental removal efficiencies. Benzene removal was again much lower than expected based on K_d. N_{ow} = 14.9 was estimated for n-butyl acetate (E = 16.8). The dispersion model predicted that the observed removal efficiencies for acetone, MEK, phenol and

Table 32. Results from Run RS4

Water flow rate = 4.66 gal/hr

Solvent flow rate = 0.790 gal/hr

Rotating disc diameter = 1.75 inch

Stator hole diameter = 2.00 inch

Rotational speed = 1430 RPM

Analytical results (concentrations in ppm):

	Acetone	Phenol	MEK	o-Cres.	n-BuAc	Benzene
Feed water	29.9	605.	124.	72.8	5457.	68.5
Product water	28.2	522.	83.3	17.0	10.8	60.4
Percent removal	5.7	13.7	22.8	76.6	99.8	11.8
Water in column	29.4	655.	114.	51.0	1324.	63.0

Measured solvent hold-up = 0.0066

Measured column temperature = 26.8°C

o-cresol should not have been possible even with an infinite value of N_{ow}. The explanation for these observations requires the consideration of interactions between solutes.

Measurements and correlations were made of the distribution coefficient for phenol distributing between water and mixtures of isobutylene and n-butyl acetate. Equation (7) provides an approximation to this more accurate but more complex correlation. In Run RS4 the feed water contained 5457 ppm of n-butyl acetate; a material balance showed that the loaded solvent contained 5.44% n-butyl acetate. The distribution coefficient for phenol thus increased from about 0.7 at the bottom of the RDC to about 3.8 at the top of the RDC. The numerical method described in Appendix C was used to quantitatively estimate the effect of n-butyl acetate on the expected removal of phenol and o-cresol.

To make this calculation we first assumed that the dispersion model with constant K_d gave a good representation of the concentration profiles for n-butyl acetate in each bulk phase. We then assumed that $N_w = N_s$ for n-butyl acetate (as has been found approximately true in several other experiments in the RDC) which, when combined with the experimental value of N_{ow} and the additivity of resistances relationship (equation 4), allowed N_w (and N_s) to be evaluated. These assumptions allowed the interfacial concentration of n-butyl acetate in the isobutylene phase to be calculated throughout the column, and thus the value of K_d for phenol was calculated. K_d was estimated to vary from 0.71 at the solvent inlet to 3.6 at the solvent outlet. We finally assume that N_w and N_s for phenol are equal to N_w and N_s determined for n-butyl acetate. Then using K_d for phenol as a function of position in the column, the numerical method discussed in Appendix C was used to calculate the concentration profile for phenol. This method led to the estimation that 23.6% of the phenol would be removed, which can be compared to the experimentally determined value of 13.7% removal. The dispersion model using K_d for phenol distributing between water and pure isobutylene predicted only 7.0% removal. Even for a case where values of K_d are thought to be nearly constant, it can be noted by observing Figure 27 that the dispersion model tends to overestimate the removal efficiency for solutes having a value of E below 1 when the assumption of additivity of resistances is used with N_w and N_s determined from solutes having values of E greater than 1.

A similar calculation was made for o-cresol by assuming equation (7) would provide a reasonable estimate of the effect of solvent composition on K_d for o-cresol. In this case there is no experimental evidence that equation (7) will be accurate. The numerical method of calculation led to the estimation that 69.1% of the o-cresol would be removed, which can be compared to the experimentally determined value of 76.6% removal and to the value using $K_d = 4.8$ of 45.3% removal. Similar calculations could have been made for acetone and MEK, but the variation of K_d with mixed solvent composition for these solutes was unknown.

For the purpose of demonstrating the effectiveness of the dual-solvent process, the results from Runs RS3 and RS4 can be combined to calculate an overall removal efficiency. By assuming that the measured removal efficiencies would be duplicated in a two-step process, the concentrations of solutes in the water phase after the n-butyl acetate extraction and after both extractions were calculated as shown in Table 33. The calculated concentrations after both extractions differ from the concentrations measured in Run RS4 since it was assumed that the water feeding the second step contained the steady state concentrations from the first step. Clearly a substantial improvement in water quality is possible by dual-solvent extraction.

In Runs RS6 and RS7 a sample of the lube oil refining waste water supplied from an industrial source was treated first by extraction using n-butyl acetate (RS6), and then by extraction using isobutylene (RS7) to recover the dissolved n-butyl acetate. As discussed in Section V, this sample differed appreciably from the typical composition of this source of waste water and from the simulated lube oil refining waste water treated in Runs RS3 and RS4. In this sample MEK was present at about 100 times its normal concentration; acetone and benzene were absent; phenol and o-cresol were present at about one-half their normal concentrations; and the suspended solid was milky grey in color rather than black as is normal. The presence of the cloudy suspended phase caused a problem in setting the rotational speed of the discs, because it was difficult to

Table 33. Calculated Effectiveness of the Dual Solvent Process

First extraction with n-butyl acetate at $F_s/F_w = 0.097$

Second extraction with isobutylene at $F_s/F_w = 0.100$

Solute	Feed Conc.	After First Extn.	After Second Ext.	Overall % Removal
Acetone	38.0	34.3	32.3	15.0
MEK	217.0	126.0	97.3	55.2
Phenol	13300.0	308.0	266.0	98.0
Benzene	169.0	30.5	26.9	84.1
o-Cresol	2107.0	25.4	5.9	99.7
n-Butyl Acetate	0.0	6110.0	12.1	---

determine at what point about 1% of the solvent appeared to be entrained in the water phase.

The feed water to Run RS6 which was treated with n-butyl acetate contained MEK (measured K_d = 4.56), phenol (K_d = 57.0, Appendix F), and o-cresol (K_d = 206, Appendix F). Because of the very high MEK concentration, two solvent flow rates were used. In Run RS6A the solvent-to-water flow ratio was about 0.1 to simulate the typical value of F_s/F_w normally used when treating this type of waste water. In Run RS6B F_s/F_w was increased to about 0.3 to provide information on how efficiently MEK could be removed during the unusual condition which caused the atypical waste water composition. The settings of the independent variables and the results of the extractions are shown in Table 34 for Run RS6A and in Table 35 for Run RS6B. The measured solvent hold-up values were very low in both these runs for an undetermined reason.

The steady-state material balance closed within less than 6% for each solute in Run RS6B, but in Run RS6A the material balance showed as much as 26% more solute entering with the feed water than leaving with the product water and loaded solvent. Inspection of the solvent-phase samples taken during the approach to steady state showed that the loaded solvent composition was still changing at the end of the experiment. Run RS6A was made following Run RS6B, and the usual practice of raising the main interface to the top of the column and then lowering it to the normal position was not followed. This meant that the solvent phase in the column above the

Table 34. Results from Run RS6A

Water flow rate = 3.21 gal/hr

Solvent flow rate = 0.369 gal/hr

Rotating disc diameter = 1.50 inch

Stator hole diameter = 2.25 inch

Rotational speed = 1100 RPM

Analytical results (concentrations in ppm):

	MEK	Phenol	o-Cresol
Feed water	12220.	8751.	892.
Product water	5883.	104.	6.5
Percent removal	51.8	98.8	99.3
Loaded solvent	48400.	66900.	6600.

n-Butyl acetate in product water = 15210 ppm.

Solvent hold-up too small to measure.

Measured column temperature = 24.2°C

Table 35. Results from Run RS6B

Water flow rate = 3.21 gal/hr

Solvent flow rate = 1.11 gal/hr

Rotating disc diameter = 1.50 inch

Stator hole diameter = 2.25 inch

Rotational speed = 1100 RPM

Analytical results (concentrations in ppm):

	MEK	Phenol	o-Cresol
Feed water	12220.	8751.	892.
Product water	2452.	77.	4.3
Percent removal	82.3	99.1	99.5
Loaded solvent	30600.	26200.	2880.

n-Butyl Acetate in product water = 15400 ppm.

Measured solvent hold-up = 0.00214

Measured column temperature = 23.4°C

interface had to be purged by the slow solvent flow during Run RS6A. Incomplete purging accounts for the lack of closure of the material balance for this run. The flow rate of the total solvent phase increased by only 1.9% in Run RS6A and 2.6% in Run RS6B as it passed through the column because the amount of solutes picked up almost exactly balanced the amount of solvent dissolved and entrained in the aqueous phase. Therefore, the analysis was calculated on a weight fraction basis using total solvent- and water-phase inlet flow rates.

The difficulty in experimentally establishing the setting for the disc rotation speed because of the turbid nature of the water-phase was previously mentioned. The chosen setting of 1100 RPM was probably higher than optimal, and because of setting the rotation speed too high a considerable amount of n-butyl acetate phase was entrained in the product water. This fact is shown by the high concentration of n-butyl acetate (> 15,000 ppm) in the product water, which is more than twice the solubility of the solvent in water. After settling for 12 hours, the concentration of n-butyl acetate had fallen to about 10,000 ppm, and after settling for 1 week, the concentration had fallen to about 7,000 ppm. Even after settling for a week the turbidity of the product water was about the same as that of the feed water.

Assuming that $G_{18} = 0.2$ as in previous experiments with n-butyl acetate as solvent, the method of Strand, et al. (1962) was used to estimate Pe_w and Pe_s, from which the values of N_{ow} listed in

Tables 36 and 37 were determined. The reason why the removal of MEK in Run RS6A was higher than what theory predicted as possible is not known, but it may be associated with the high concentration of MEK in both phases. The MEK removal would have had to be 42.9% rather than the measured 51.8% to give $N_{ow} = 5.5$, as expected from the results on Run RS6B. By assuming $G_{18} = 0.2$ the solvent hold-up was predicted as 0.0088 for RS6A and 0.0272 for RS6B, which are much larger than the measured values listed in Tables 34 and 35. The maximum stable drop diameter predicted with $G_{18} = 0.2$ was about equal to the observed value.

When the data from Run RS6B were evaluated in terms of a straight line plot of $1/N_{ow}$ vs $1/E$, $N_w = 11$ and $N_s = 7.7$ were estimated as the individual-phase numbers of transfer units. From the data from Run RS6A N_w was estimated to be about 11, but N_s could not be estimated.

In Run RS7 the collected water which had been treated by n-butyl acetate extraction in RS6 was treated by extraction with isobutylene at a low solvent-to-water flow ratio ($F_s/F_w = 0.102$). The major solutes were n-butyl acetate ($K_d = 168$ Appendix E) and MEK ($K_d = 2.49$, Appendix E) with smaller smounts of phenol ($K_d = 0.7$, Appendix E) and o cresol ($K_d = 4.8$, Appendix E). The water treated by n-butyl acetate extraction in Run RS6A was treated with isobutylene in Run RS7A, and the water treated in RS6B was treated with isobutylene

Table 36. Experimental Estimates of N_{ow} for Run RS6A

	MEK	Phenol	o-Cresol
E	0.46	5.76	20.8
% Removal	51.8	98.8	99.3
N_{ow}	∞	12.5	10.7

G_{18} assumed to be 0.2; $Pe_w = 4.26$

and $Pe_s = 22.1$

Table 37. Experimental Estimates of N_{ow} for Run RS6B

	MEK	Phenol	o-Cresol
E	1.39	17.3	62.7
% Removal	79.9	99.1	99.5
N_{ow}	5.5	10.2	11.1

G_{18} assumed to be 0.2; $Pe_w = 4.36$

and $Pe_s = 21.9$

in RS7B. The settings of independent variables and the results of the treatment are shown in Tables 38 and 39. The removal efficiencies were very similar in the two runs with a slightly better result in RS7A. The results were also very similar to those in Run RS4 (Table 32) where a simulated waste water was used. The solvent hold-up measured in these two experiments was about 5 times as large as that measured in RS4. The material balance closures were within 12% in both runs.

When this waste water was treated by n-butyl acetate extraction in RS6, no appreciable improvement in turbidity occurred. However, during the extractions using isobutylene in RS7, the milky grey suspended phase was greatly reduced. The suspended phase may have been particles of wax which were more soluble in or possibly more readily coalesced with the isobutylene droplets than with n-butyl acetate droplets.

When the measured solvent hold-up was used to estimate G_{18} and the droplet diameter, very low values for G_{18} (0.024 - 0.026) and d_p (0.0022 - 0.0024 inch) were calculated. With $G_{18} = 0.337$, as was found with the simulated water in RS4, values of d_p agreed with those visually estimated, but the calculated hold-up was much below the measured values.

Values of N_{ow} were calculated for each solute using $G_{18} = 0.337$, which gave $Pe_w = 3.55$ and $Pe_s = 32.5$, and using K_d for each solute as though the solvent were pure isobutylene. As expected this calculation predicted that only n-butyl acetate could possibly have been removed to the extent measured. This

Table 38. Results from Run RS7A

Water flow rate = 3.21 gal/hr
Solvent flow rate = 0.553 gal/hr
Rotating disc diameter = 1.75 inch
Stator hole diameter = 2.00 inch
Rotational speed = 1450 RPM

Analytical results (concentrations in ppm):

	Phenol	MEK	o-Cresol	n-Butyl Acetate
Feed water	306.	5573.	24.2	7133.
Product water	227.	3597.	2.3	11.0
Percent removal	25.8	35.5	90.5	99.8

Measured solvent hold-up = 0.0362
Measured column temperature = 23.3°C

Table 39. Results from Run RS7B

Water flow rate = 3.21 gal/hr

Solvent flow rate = 0.553 gal/hr

Rotating disc diameter = 1.75 inch

Stator hole diameter = 2.00 inch

Rotational speed = 1450 RPM

Analytical results (concentrations in ppm):

	Phenol	MEK	o-Cresol	n-Butyl Acetate
Feed water	229.	2801.	18.0	6791.
Product water	190.	1891.	2.8	15.2
Percent removal	17.0	32.5	84.4	99.8

Measured solvent hold-up = 0.0346

Measured column temperature = 23.3°C

calculation gave N_{ow} = 19.1 in Run RS7A and N_{ow} = 17.3 in Run RS7B for n-butyl acetate. The numerical calculation described for Run RS4 and in Appendix C was used to estimate the removal efficiencies of phenol and o-cresol predicted from the effect that n-butyl acetate in the isobutylene phase has on the values of K_d for these two solutes. This calculation, made assuming $N_s = N_w$ for n-butyl acetate, led to the prediction that 27.4% of the phenol and 72.6% of the o-cresol should have been removed. These results are in reasonably good agreement with the experimental values.

The chemical oxygen demand (COD) was determined for the initial waste water used as feed in RS6 and for the product solutions from RS7A and RS7B. In Table 40 these results are compared to values of theoretical oxygen demand (TOD) calculated from the concentrations of MEK, phenol, o-cresol, and n-butyl acetate. The agreement between COD and TOD is remarkably good.

As was done previously in Runs RS3 and RS4, the effectiveness of the dual solvent process was estimated by calculating overall removal efficiencies. The results for the combination RS6A and RS7A and for the combination RS6B and RS7B are shown in Table 41. In these calculations the n-butyl acetate which was present as a dispersed phase after the first extraction was assumed to be completely removed without affecting the removal of dissolved solutes in the second extraction. This assumption was necessary since no time would be provided for phase separation between the two steps. The presence of a high

Table 40. COD and TOD for Runs RS6 and RS7

	COD (ppm)	TOD (ppm)
Feed to RS6	54,450	52,900
Product from RS7A	8,572	9,350
Product from RS7B	4,692	5,110

Table 41. Overall Removals for the Dual Solvent Process

First extraction with n-butyl acetate.

Second extraction with isobutylene.

	Feed Conc.	After First Extn.	After Second Extn.	Overall % Removal
Runs RS6A and RS7A:				
		(F_s/F_w = 0.101)	(F_s/F_w = 0.102)	
MEK	12220.	5883.	3795.	68.9
Phenol	8751.	104.	77.2	99.1
o-Cresol	892.	6.5	0.6	99.9
n-Butyl Acetate	0.	15210.	11.0	---
TOD	52900.	48150.	9470.	82.1
Runs RS6B and RS7B:				
		(F_s/F_w = 0.304)	(F_s/F_w = 0.102)	
MEK	12220.	2452.	1655.	86.5
Phenol	8751.	77.0	63.9	99.3
o-Cresol	892.	4.3	0.7	99.9
n-Butyl Acetate	0.	15400.	15.2	--
TOD	52900.	40120.	4230.	92.0

TOD as well as the cost of lost n-butyl acetate can be seen to provide the need for a second extraction with the volatile solvent. The improvement in final product by operating the first extraction with a higher solvent flow rate is also illustrated by comparing the results for the two combinations of runs.

In Runs RS8 and RS9 a mixture of about 50 weight percent n-butyl acetate and 50 weight percent isobutylene was used to treat samples of lube oil refining waste water. These experiments provide information relating to a dual solvent process with linked solvent cycles. The second step in this dual solvent process utilizing isobutylene extraction for n-butyl acetate recovery is similar to isobutylene extraction in a dual solvent process with separate solvent cycles. Therefore, the data from Runs RS4 and RS7 apply directly, and the second step in the process with linked solvent cycles was not simulated.

In Run RS8 a mixture of 48.7 weight % n-butyl acetate and 51.3 weight % isobutylene was used to treat a sample of industrial lube oil refining waste water. If we assume that the distribution coefficient for each solute between water and the solvent mixture was given by equation (7) as was found to be valid experimentally for phenol, then an approximate value for K_d can be determined for each solute. The solutes which were present included acetone (K_d = 0.83), MEK (K_d = 3.50), phenol (K_d = 28.1), o-cresol (K_d = 100), and benzene (K_d = 239).

It was assumed that the physical properties of the mixed solvent would be intermediate between the properties of the two pure solvents. Therefore, the column was set up with the smaller set of discs (1.50 inch) which had been used for n-butyl acetate extractions and with the stators having the smaller holes (2.00 inch) which had been used for isobutylene extraction. The initial flow settings were chosen so that F_s/F_w was about 0.2; a dual solvent process with linked solvent cycles with $F_s/F_w = 0.2$ in the initial extraction step (50 weight % of each solvent) and with $F_s/F_w = 0.1$ in the second extraction step (pure volatile solvent) should be comparable to a dual solvent process with separate solvent cycles with $F_s/F_w = 0.1$ in each pure solvent extraction step. The settings of the independent variables and the results of this extraction are shown in Table 42.

A problem which was encountered due to flow line plugging during this run resulted in a gradual decrease in both the solvent and the water flow rates. For this reason a range of flow rates is given in Table 42; the higher number is the initial setting, and the lower number is the final setting. These decreasing flows made calculation of the steady state material balance inaccurate and caused the solvent hold-up measurement to be invalid. However, the measured removal efficiencies are believed to be a good approximation of the efficiencies which would have been measured at the median of the ranges of flow rates. The values of E reported were calculated at median flows. The COD of the feed and product water streams was not determined.

Table 42. Results from Run RS8

Water flow rate = 3.92 - 4.16 gal/hr

Solvent flow rate = 1.055 - 1.200 gal/hr

Solvent feed composition = 48.7 weight % n-butyl acetate in isobutylene

Rotating disc diameter = 1.50 inch

Stator hole diameter = 2.00 inch

Rotational speed = 1090 RPM

Analytical results (concentrations in ppm):

	Acetone	MEK	Phenol	o-Cresol	Benzene
Feed water	24.6	108.	17170.	2660.	36.9
Product water	12.1	54.9	1902.	124.	9.2
Percent removal	50.8	49.2	88.9	95.3	75.1
E	0.17	0.72	5.76	20.5	49.0

n-Butyl acetate in product water = 2364 ppm.

Measured column temperature = 21.2°C

Estimated maximum drop diameter = 0.06 inch

The comparison of results from Run RS8 with the prediction from the method of Strand, et al. (1962) was based on choosing G_{18} from the observed maximum stable drop size and from the observed hold-up measured for the same system in Run RS9 (reported below). Using $G_{18} = 0.17$ as the chosen value resulted in the values of Pe_w, Pe_s, and N_{ow} for each solute shown in Table 43. The infinite value of N_{ow} for acetone is undoubtedly the result of a large analytical error either for the feed or the product water stream. For a reasonable value of $N_{ow} = 0.5$, only 15.2% removal would be expected. The values of N_{ow} for MEK, phenol, and o-cresol fell on a straight line when plotted as $1/N_{ow}$ vs. $1/E$ resulting in $N_w = 4.4$ and $N_s = 3.3$ as estimates for the individual-phase numbers of transfer units. As in previous extractions, the removal of benzene was much less efficient than predicted from its high value of E.

The appearance of the column during Run RS8 was similar to the appearance in Runs RS1A and RS1B. In those previously described runs, we found that the column operation was greatly improved by converting to larger discs and to stators with smaller holes. This modification in column geometry was more successful in improving the contact between solvent and water than could be achieved by simply increasing the rotational speed. Apparently the hydrodynamics of the mixed solvent system is more nearly like extraction with pure isobutylene than extraction with pure n-butyl acetate. Therefore, the column might operate better using the 1.75-inch discs and the stators with 2.00-inch holes.

Table 43. Experimental Estimates of N_{ow} for Run RS8

	Acetone	MEK	Phenol	o-Cresol	Benzene
E	0.17	0.72	5.76	20.5	49.0
% Removal	50.8	49.2	88.9	95.3	75.1
N_{ow}	∞	1.5	3.4	4.6	1.7

F_{18} assumed to be 0.17; $Pe_w = 6.59$ and $Pe_s = 33.8$

In Run RS9 a mixture of 53.1 weight % n-butyl acetate and 46.9 weight % isobutylene was used to treat a prepared water stream which contained MEK and phenol. The larger discs were used to determine if the operation would be improved over that in Run RS8, and the appearance of the column as well as the rates of mass transfer showed that improvement was indeed achieved. The droplets of mixed solvent were smaller, and the hold-up was larger when using the larger discs. However, no increase in the amount of solvent entrained with the product was noted with the larger discs.

The settings of the independent variables and the results of the extraction with mixed solvent in Run RS9 are shown in Table 44. F_s/F_w was set at about 0.2 as in Run RS8. If we again assume that the distribution coefficient for each solute between water and the mixed solvent was given by equation (7), then $K_d = 3.59$ for MEK and $K_d = 30.6$ for phenol. The steady state material balance closed within 8% for both solutes.

In the comparison of the results from Run RS9 with the prediction from the method of Strand, et al. (1962), G_{18} calculated from the measured solvent hold-up agreed with G_{18} estimated from the measured maximum droplet diameter. Using this $G_{18} = 0.17$ resulted in $Pe_w = 6.54$ and $Pe_s = 25.9$ and in $N_{ow} = 12.2$ for phenol. The observed 78.5% removal for MEK was higher than would be predicted even with an infinite value of N_{ow}; this probably reflects a failing in the method for estimating K_d for the mixed solvent.

Table 44. Results from Run RS9

Water flow rate = 4.66 gal/hr

Solvent flow rate = 1.364 gal/hr

Solvent feed composition = 53.6 weight % n-butyl acetate in isobutylene

Rotating disc diameter = 1.75 inch

Stator hole diameter = 2.00 inch

Rotational speed = 1090 RPM

Analytical results (concentrations in ppm):

	MEK	Phenol
Feed water	424.	17320.
Product water	91.3	93.4
Percent removal	75.5	99.5
Water in column	323.	8762.
E	0.78	6.68

n-Butyl acetate in product water = 2593 ppm.

Measured solvent hold-up = 0.0238

Measured column temperature = 22.3°C

Estimated maximum drop diameter = 0.03 inch

For a reasonable N_{ow} = 6 with E = 0.78, 66.0% removal of MEK would be expected. The observed 99.5% removal for phenol was the highest value measured for the removal of phenol in any experiment reported for this water.

Summary of Experiments on Lube Oil Refining Waste Water.

In Runs RS2, RS3, and RS6 n-butyl acetate was used to treat simulated and actual samples of lube oil refining waste water. The operation of the RDC was similar in these runs except that the rotational speed was higher in RS6, which resulted in some solvent entrainment. The method of Strand, et al. (1962) gave an adequate correlation of observed drop sizes when G_{18} = 0.2 was used. By using this monodisperse drop size model, the correlations discussed in Section V for mass transfer toward stagnant drops, circulating drops, and drops in a turbulent continuous phase (Calderbank and Moo-Young, 1961) were used to calculate values of N_w. These theoretical estimates of N_w are compared in Table 45 to the experimental values which were determined by plotting $1/N_{ow}$ vs 1/E. The ratio of N_w predicted by the model for drops in a turbulent continuous phase to the experimental value of N_w varied from 0.27 to 1.0, with 0.5 as found in Test Run RS13 being an average value. These are not sufficient data for a clear choice of this model over those for stagnant or circulating drops, but for the purpose of estimating costs on a larger scale they should be useful. Theoretical and experimental estimates of N_s are also listed in Table 45. The ratio of N_s predicted for stagnant drops to N_s

Table 45. Theoretical and Experimental Mass Transfer Estimates for Extraction with n-Butyl Acetate

Run number	RS2	RS3	RS6B
N (RPM)	617	805	1100
Pe_w	8.53	9.55	4.35
Pe_s	27.8	29.2	21.9
Experimental N_w	2.5	7.3	11.0
N_w for turbulent transfer	1.1	2.0	11.3
N_w for stagnant drops	0.8	1.0	4.0
N_w for circulating drops	8.1	14.0	66.0
Experimental N_s	2.4	8.4	7.7
N_s for stagnant drops	5.6	15.0	29.0
N_s for circulating drops	17.7	34.9	54.0

estimated from $1/N_{ow}$ vs 1/E plots varied from 1.8 to 3.7, with 2.6 as found in Test Run RS13 being an average value. The fact that the experimental estimates for N_s are even less than for stagnant drops may be an artifact of the assumption of monodisperse drops. Variations in drop size and in the intensity of mixing in the continuous phase surrounding the drops can cause the ratio of individual-phase mass transfer coefficients to be different in different locations within the contactor. King (1964) has described how a variation in the ratio of individual-phase mass transfer coefficients over the total interface can have this effect.

The regeneration of the loaded n-butyl acetate from these runs was carried out in a glass, batch distillation column at atmospheric pressure. The separation between the phenolics and n-butyl acetate was very easy to make. The separation between n-butyl acetate and benzene was more difficult, but was possible. The separation between MEK and n-butyl acetate was of intermediate difficulty. These qualitative results should also apply to continuous distillations.

In Runs RS1, RS4, and RS7, isobutylene was used to recover n-butyl acetate from actual and simulated samples of lube oil refining waste water. The hydrodynamic behavior of the column was greatly improved by replacing the 1.50-inch discs and stators with 2.25-inch holes with a set of 1.75-inch discs and stators with 2.00-inch holes. Using the method of Strand, et al. (1962) with $G_{18} = 0.337$ gave a good representation of observed drop sizes and solvent hold-up. Based on the removal efficiency for n-butyl acetate, the ratio of N_w from the turbulent mass transfer model (Calderbank and Moo-Young, 1969) to N_w estimated experimentally ranged from 0.06 to 0.13, with the lower value occurring more often. The value of N_s could not be determined experimentally because of interactions between solutes, but $N_w = N_s$ seemed to give a reasonable estimate.

The regeneration of isobutylene was carried out continuously during these experiments, but the very low production rate of recovered solutes made quantitative evaluation difficult. The separation of isobutylene from n-butyl acetate was very easy, and MEK was the only solute that could be detected in the regenerated isobutylene.

In Runs RS8 and RS9 mixtures of n-butyl acetate and isobutylene were used to treat actual and simulated lube oil refining waste water. The operation of the column was best when using the same set of discs and stators used for pure isobutylene extraction, and the hydrodynamics could be correlated by using $G_{18} = 0.17$ for mixtures of solvent near 50% n-butyl acetate. The ratio of N_w predicted for turbulent mass transfer to N_w predicted from the $1/N_{ow}$ vs. $1/E$ plots varied from 0.5 to 0.8, with the larger value corresponding to the higher removal efficiencies in Run RS9. In RS8 where N_s could be estimated, the ratio of N_s predicted for stagnant drops to that estimated experimentally was about 6.

The loaded mixed solvent was distilled continuously during each experiment, but the temperature of the Freon 114 heat source was not high enough to remove more than about half the isobutylene. The remaining isobutylene and all the n-butyl acetate were removed and distilled in the atmospheric batch apparatus. About half the isobutylene was thus lost. The isobutylene which was recovered contained almost no (< 10 ppm) n-butyl acetate. The batch distillation produced very pure n-butyl acetate for recycle except for a small amount of benzene which was difficult to separate.

In all three types of extraction steps when treating actual and simulated lube oil refining waste water, the removal of benzene is much lower than predicted based on its high value of K_d.

Experiments on Ethylene Quench Waste Water.

In Runs RS10 and RS11 samples of ethylene quench waste water were treated with isobutylene and isobutane, respectively. All the solutes present in this polluted water were not identified; the only individual pollutants whose concentrations were measured were benzene, toluene, xylenes (o-, m-, and p-xylene plus ethylbenzene), and phenol. The COD of the feed and product waters was also measured. Only processes with a single, volatile solvent were simulated since the low concentration of phenol did not appear to justify the added cost of a dual solvent process.

In Run RS10 isobutylene was used to treat ethylene quench water at a low solvent-to-water flow ratio (F_s/F_w = 0.101). The principal solutes were benzene (K_d = 407), toluene (K_d ≈ 1690), and phenol (K_d = 0.7, Appendix E). The distribution coefficient for toluene was estimated from K_d for benzene by correcting for differences in their water solubilities and their solubility parameters. The settings of the parameters and results are shown in Table 46. The material balance closures for each solute were within 12%.

In Run RS11 isobutane was used to treat ethylene quench water at a low flow ratio (F_s/F_w = 0.097). The principal solutes were benzene ($K_d \approx 338$), toluene ($K_d \approx 1460$), and phenol (K_d = 0.2, Appendix E). The distribution coefficients for benzene and toluene were estimated by correcting K_d for benzene between water and isobutylene. The settings of the parameters and the results are shown in Table 47. The material balance closures for each solute were within 15%.

The major difference in results between Runs RS10 and RS11 was an observation that the turbidity of the feed water was reduced more dramatically by isobutane extraction. The turbidity of feed and product waters in Run RS11 was determined by using a laboratory turbidimeter (Hach Chemical Company, Model 1860A); a 72% reduction in turbidity was measured. The turbidities of feed and product waters in Run RS10 were not measured, but by visual inspection no significant improvement in turbidity occurred by isobutylene extraction. The ability of isobutane to extract the dispersed solids and liquids which caused the turbidity was probably the reason for a greater COD reduction with isobutane extraction (58%) than with isobutylene extraction (35%).

Table 46. Results from Run RS10

Water Flow Rate = 4.62 gal/hr

Isobutylene Flow Rate = 0.786 gal/hr

Rotating Disc Diameter = 1.75 inch

Stator Hole Diameter = 2.00 inch

Rotational Speed = 1450 RPM

Analytical Results (concentrations in ppm):

Solute	Feed	Product	% Removal	In Column
Benzene	71.1	2.9	95.9	6.6
Toluene	40.5	2.3	94.3	4.3
Xylenes	40.3	<1	>97	7.1
Phenol	66.9	63.1	5.7	66.1

Measured Solvent Hold-up = 0.0217

Estimated Maximum Stable Drop Diameter = 0.05 inch

Column Temperature = 20.8°C

	Feed	Product
Measured COD (ppm)	1880	1209
Calculated COD (ppm)	632	166

Table 47. Results from Run RS11

Water Flow Rate = 4.60 gal/hr

Isobutane Flow Rate = 0.786 gal/hr

Rotating Disc Diameter = 1.75 inch

Stator Hole Diameter = 2.00 inch

Rotational Speed = 1450 RPM

Analytical Results (concentrations in ppm):

Solute	Feed	Product	% Removal	In Column
Benzene	81.2	2.4	97.0	10.6
Toluene	43.8	1.6	96.3	5.1
Xylenes	33.6	<1	>97	6.9
Phenol	68.2	66.0	3.2	66.5

Measured Solvent Hold-up = 0.00961

Estimated Maximum Stable Drop Diameter = 0.05 inch

Column Temperature = 23.4°C

	Feed	Product
Measured COD (ppm)	1880	699
Calculated COD (ppm)	655	169
Measured Turbidity (FTU)*	142	40

* FTU = Formazin Turbidity Units

The comparison of results from Runs RS10 and RS11 with the predictions from the method of Strand, et al. (1962) was based on choosing G_{18} from the observed maximum stable drop size. The Peclet numbers and the values of N_{ow} are shown in Table 48. The removal efficiencies and values of N_{ow} for benzene and toluene were slightly larger in Run RS11 than in RS10; this was probably due to a slightly better solvent dispersion. The removal efficiency for phenol was better in RS10 because of the higher value of K_d. The value of N_{ow} for toluene was lower than for benzene because the diffusivity of toluene in water is lower; since the resistance to mass transfer for these two solutes lay almost entirely in the water phase, the higher value of K_d for toluene had little influence on N_{ow}. The ratio of N_w predicted by the model of Calderbank and Moo-Young (1961) to N_{ow} ($\approx N_w$) determined experimentally for benzene and toluene ranged from 0.51 to 0.60; no comparison of theory to experiment could be made for N_s.

In both runs the volatile solvent was continuously regenerated by distillation. The analysis of regenerated solvent failed to show any trace of benzene, toluene, or phenol. This indicated that both volatile solvents could be regenerated with ease.

Experiments on Oxychlorination Waste Water.

In Runs RS5 and RS12 samples of neutralized oxychlorination waste water were treated with isobutylene and 2-ethyl hexanol, respectively. Additional

Table 48. Experimental Estimates of N_{ow} for Each Solute in Runs RS10 and RS11

	RS10	RS11
G_{18}	0.22	0.20
Pe_w	4.94	5.04
Pe_s	27.3	28.8
F_s/F_w	0.1010	0.0973
E for Benzene	41.1	32.9
Benzene % Removal	95.9	97.0
N_{ow} for Benzene	5.1	5.8
E for Toluene	171	142
Toluene % Removal	94.3	96.3
N_{ow} for Toluene	4.3	5.0
E for Phenol	0.070	0.019
Phenol % Removal	5.7	3.2
N_{ow} for Phenol	∞	∞

experiments with this type of waste water are described in Appendix I.

The sample of oxychlorination waste water which was treated by isobutylene extraction in Run RS5 had been neutralized by addition of solid NaOH. As described in Section V it was later determined that this method led to decomposition of about 15% of the chloral to form chloroform and sodium formate. Run RS5 had to be terminated before steady state was reached because of a failure of one of the shaft bearings, but it was estimated that about 95% of the 3140 ppm of ethylene dichloride in the feed and about 60% of the 1700 ppm chloroform in the feed would be removed at an intermediate flow ratio ($F_s/F_w = 0.2$). Essentially none of the ethanol, ethylene chlorohydrin, or undecomposed chloral was removed during treatment with isobutylene.

In Run RS12 a sample of oxychlorination waste water which had been neutralized by adding $NaHCO_3$ was extracted with 2-ethyl hexanol at a low flow ratio ($F_s/F_w = 0.106$). The settings of independent variables and the results are shown in Table 49. In addition to the organic pollutants in the feed waste water, 9.26 weight % NaCl remained from the neutralization of the HCl. The presence of this high a salt concentration made quantitative analysis for this run difficult.

Measurements were made of the distribution coefficient for chloral hydrate distributing between 2-ethyl hexanol and both salt-free and salt-containing waste water. We found $K_d = 50$ for chloral hydrate in

Table 49. Results from Run RS12

Water Flow Rate = 4.32 gal/hr

Solvent Flow Rate = 0.551 gal/hr

Rotating Disc Diameter = 1.50 inch

Stator Hole Diameter = 2.25 inch

Rotational Speed = 800 RPM

Analytical Results (concentrations in ppm):

Solute	Feed	Product	% Removal	In Column
Ethanol	286	265	7.3	303
Ethylene Dichloride	1505	<20	>99	503
Ethylene Chlorohydrin	1636	1292	21.0	1472
Chloral Hydrate	15220	7726	49.2	10610

2-Ethyl Hexanol in Product Water = 374 ppm

Column Temperature = 22.2°C

Measured Solvent Hold-up = 0.0156

pure water and K_d = 146 for chloral hydrate in 10% NaCl solution. From these data the value of K_d for chloral hydrate in RS12 was about 140. The value of K_d for ethanol distributing between pure water and sec-octanol is about 0.83 (Krishnamurty and Rao, 1954), so the value in RS12 was estimated to be about 1. The value of K_d for ethylene dichloride between pure water and isobutylene is 70.0, so the value in RS12 was probably about 200 for this polar solvent. A value for K_d for ethylene chlorohydrin was back calculated from the results on RS12 giving $K_d \simeq 5$.

Using the method of Strand, et al. (1962), G_{18} = 0.13 was estimated from the measured solvent hold-up. As with runs using n-butyl acetate as solvent, the hold-up appeared to increase just below the mid-column bearing. A value of G_{18} = 0.20 gave a drop diameter closer to that estimated visually, but there is not enough information available from this one run to make a choice between these two values of G_{18}.

Although the uncertainty in values for K_d makes any comparison between theory and experiment meaningless for this run, several conclusions can be reached by comparing one solute to the others and by comparing theoretical estimates for this run with estimates for other runs. By comparing the removal efficiencies for the two solutes with large values of E, ethylene dichloride and chloral hydrate, it is clear that something caused a significant difference. This result is also clear by comparing the experimental values for N_{ow} with calculated values for N_{ow}

determined by calculating N_w from the turbulent mass transfer model and N_s from the stagnant drop model using 0.13 for G_{18}. The experimental values of N_{ow} for ethylene dichloride and chloral hydrate are 7.0 and 0.75, respectively, while the calculated values are 6.4 and 5.5, respectively. The experiment described in Appendix I clearly shows that chloral hydrate undergoes a slow chemical reaction in addition to simple mass transfer, which explains this difference.

Another conclusion can be made by comparing N_w calculated from the turbulent mass transfer model with N_s calculated from the stagnant drop model. In all previous runs, the calculated value for N_s was 5 to 15 times larger than the calculated value for N_w, while for this run the calculated values are about equal. The explanation for this difference is related to the high viscosity of 2-ethyl hexanol (i.e., about 8 cp). When 2-ethyl hexanol is used as solvent, the relative importance of the solvent-phase resistance to mass transfer will be increased. This will affect the removal of ethanol and ethylene chlorohydrin most seriously.

Experiments on Phenol-Formaldehyde Resin Manufacture Wastewater

Table 50 reports results from Run RS15, made using a mixed solvent of n-butyl acetate and isobutylene for extraction of the wastewater from phenol-formaldehyde resin manufacture. The disc and stator combination used was that which had proven to be most successful for mixed-solvent treatment of the lube-oil refining wastewater. The flow ratio was $F_s/F_w = 0.206$, to allow comparison with a pure butyl-acetate run where the flow ratio was on the order of 0.1. The three solutes monitored were methanol ($K_d = 0.10$, measured), formaldehyde ($K_d = 0.15$, measured), and phenol ($K_d = 6.15$, measured). All these reported K_d values are for the feed water concentration and for no other solutes present. Values of K_d are, in fact, highly variable with respect to solute concentration, and with respect to the concentrations of other solutes in the system. The observed % removal of phenol is very high under these conditions, while the observed % removals of methanol and formaldehyde are quite low.

Table 51 gives results from Run RS16, where pure n-butyl acetate was used as solvent for treating the same wastewater, this time with a flow ratio $F_s/F_w = 0.12$. The flow ratio could not be made lower because of the need to maintain a sufficient density difference between phases as phenol built up in the solvent phase. The density of pure butyl acetate is 0.882 g/cm^3; that of pure phenol is 1.071 g/cm^3. The disc and stator combination is that used successfully in other experiments with pure butyl acetate solvent. Under these conditions K_d for phenol at the feed concentration is 12.0. The observed % removal of phenol is lower than

Table 50. Results from Run RS15

Wastewater from Phenol-Formaldehyde Resin Manufacture

Solvent: 48.2 wt % n-butyl acetate, 51.8 wt % isobutylene

Water Flow Rate = 2.41 gal/hr

Solvent Flow Rate = 0.677 gal/hr

Rotating Disc Diameter = 1.75 inch

Stator Hole Diameter = 2.00 inch

Rotational Speed = 1200 RPM

Column Temperature = 22.7°C

Analytical Results (concentrations in ppm):

Solute	Feed	Product	% Removal
Methanol	12,000	11,510	4.1
Formaldehyde	17,370	16,450	5.3
Phenol	48,270	483	99.0

Table 51. Results from Run RS16

Wastewater from Phenol-Formaldehyde Resin Manufacture

Solvent: n-Butyl Acetate

Water Flow Rate = 2.18 gal/hr
Solvent Flow Rate = 0.295 gal/hr
Rotating Disc Diameter = 1.50 inch
Stator Hole Diameter = 2.25 inch
Rotational Speed = 1250 RPM
Column Temperature = 23.4°C

Analytical Results (concentrations in ppm):

Solute	Feed	Product	% Removal
Methanol	12,000	7,608	36.6
Formaldehyde	17,370	10,370	40.3
Phenol	48,270	6,082	87.4

in the mixed-solvent run (87.4% vs. 99.0%), but the % removals of methanol and formaldehyde (37% and 40%, respectively) are much higher than in the mixed-solvent run.

It is interesting to explore the reasons for the very different removals of the various solutes in the two different runs. In the mixed-solvent run, much of the phenol extraction occurs with a much higher equilibrium distribution coefficient than that prevailing at the feed concentration, since the distribution coefficient is much higher at lower concentrations of phenol in the aqueous phase (see Appendix F). Consequently there is a very high % removal of phenol. For methanol and formaldehyde the extraction factors are quite low, of the order of E = 0.02 to 0.03, based upon the equilibrium distribution coefficients for these components into the solvent (in the absence of phenol). These values of the extraction factor would correspond to expected removals in the range of 2 to 3%, somewhat lower than the values of 4 to 5% observed. The somewhat larger actual percentage removals probably result from the solvent power of the phenol which builds up in the solvent. A mass balance on phenol indicates that there is about 19% phenol in the exit solvent. This would be sufficient to increase the equilibrium distribution coefficients for methanol and formaldehyde significantly.

The lower removal of phenol and the higher removals of methanol and formaldehyde in the pure n-butyl-acetate solvent run (RS16) can be rationalized on the basis of the still higher build-up of phenol in the solvent phase because of the lower flow ratio. A mass balance on phenol indicates that the phenol builds up in the exit solvent phase to a level of about 25%, while methanol and formaldehyde build up to levels of 3 and 4%, respectively. The higher concentration of phenol in the exit solvent will reduce the equilibrium distribution coefficient of phenol at the solvent-exit, water-inlet end of the column, thereby causing a "pinch" situation in the operating diagram, which serves to reduce the separation of phenol attainable. At the same time, the higher concentration of phenol in the solvent phase should serve to increase the equilibrium distribution coefficients for methanol and formaldehyde substantially, and the presence of significant amounts of methanol in the solvent may further increase the distribution coefficient for formaldehyde, and vice versa, since these two molecules can interact strongly through hydrogen bonding:

$$H_3C - O - H --- O = CH_2$$

These results imply that one can trade-off between the percent removals of phenol and of methanol and formaldehyde in extraction of this wastewater by adjusting the solvent to water ratio and thereby altering the extent to which the solutes build up in the solvent phase.

The very complex interactions between the solutes and their high levels of concentration preclude any reliable analysis of the mass-transfer behavior of the extractor in these runs.

Experiments on Hydrofiner Condensate Wastewater

Table 52 presents results of Run RS17, where methyl isobutyl ketone (MIBK) was used as a solvent to treat the hydrofiner condensate wastewater. The disc and stator sizes correspond to those used for butyl acetate runs with other waters. The flow ratio chosen was $F_s/F_w = 0.125$. The one peak which was monitored was that of phenol (measured $K_d = 68$), for which the removal was better than 99.8%. The removal cannot be determined more precisely since the limit of quantitative detection of the chromatographic analysis method is about 1 ppm, and the level of phenol in the effluent water was below that level. Other organic components were present at similarly low levels, and the chromatographic method was not sufficiently sensitive to monitor their removal.

The extraction with MIBK serves to leave considerable (15,700 ppm) MIBK in the product water. This corresponds to about 42,500 ppm of COD; hence a COD measurement for the exit water reflects primarily the MIBK content and does not give information on the degree of removal of other constitutents. Of course, the large residual amount of MIBK in the exit water could be removed efficiently by a subsequent extraction with isobutylene or isobutane.

Table 53 shows results for Run RS18, where a mixed solvent of MIBK and isobutylene was used to extract the hydrofiner condensate at a phase flow ratio of $F_s/F_w = 0.209$. The disc and stator combination was the same as used previously for mixed solvents. Again the removal of phenol is so large that the amount of phenol left in the effluent water cannot be reliably detected. The amount of MIBK left in the product water

Table 52. Results from Run RS17

Wastewater: Hydrofiner Condensate
Solvent: Methyl Isobutyl Ketone

Water Flow Rate	= 3.93 gal/hr
Solvent Flow Rate	= 0.617 gal/hr
Rotating Disc Diameter	= 1.50 inch
Stator Hole Diameter	= 2.25 inch
Rotational Speed	= 1250 RPM
Column Temperature	= 24.5°C

Analytical Results (Concentrations in ppm):

Solute	Feed	Product	% Removal
Phenol	400	<1	>99.8%

COD of feed water = 17,530 ppm
MIBK Concentration in Product Water = 15,680 ppm (42,500 ppm COD)

Table 53. Results from Run RS18

Wastewater: Hydrofiner Condensate

Solvent: 49.5 wt % Methyl Isobutyl Ketone;
50.5 wt % isobutylene

Water Flow Rate = 2.50 gal/hr
Solvent Flow Rate = 0.753 gal/hr
Rotating Disc Diameter = 1.75 inch
Stator Hole Diameter = 2.00 inch
Rotational Speed = 1150 RPM
Column Temperature = 24.2°C

Analytical Results (concentrations in ppm)

Solute	Feed	Product	% Removal
Phenol	400	<1	> 99.8

COD of Feed Water = 17,530 ppm
COD of Product Water = 18,530 ppm
MIBK Content of Product Water = 3150 ppm (9000 ppm COD)

is much less for the mixed-solvent case (3150 ppm, as compared to 15,700 ppm for pure MIBK solvent), and hence contributes less to the COD of the product water. Subtracting an estimated 9000 ppm for the contribution of the MIBK, the COD of remaining constituents of the effluent water is about 9,500 ppm. This corresponds to removal of about 46% of the COD from the constituents of the original water. As was indicated in Section V, it is expected that most of the original COD is attributable to H_2S, which would be removed by a stripping process. Again, the residual MIBK could readily be removed by a subsequent extraction with isobutane or isobutylene.

Experiments on Wastewater from Styrene Manufacture

Pure isobutylene was used as the solvent for extraction of the wastewater from styrene manufacture, since the components known to be present were all aromatics, with very high distribution coefficients into isobutylene. Table 54 reports experimental results for the extraction of this water with isobutylene. The combination of 1.75-inch discs and 2.00-inch stators was employed, so as to give visually good dispersion.

Comparison of the feed concentrations with those originally measured for this water (p. 78) shows an appreciable loss of the various components during a few months' storage.

The mass flow ratio of solvent to feed water (F_s/F_w) was 0.107. For benzene (K_d = 407, measured), the extraction factor (K_dF_s/F_w) was therefore 43.5. Values of K_d for ethylbenzene and styrene were not measured, but would be expected to be greater than K_d for benzene, because of the additional hydrocarbon groups on the molecule. Hence for all three solutes the extraction factor was quite high, and may to a good approximation be considered infinite for purposes of interpreting the mass-transfer behavior.

The percentage removals observed for the three components in this extraction run are all high, and are in line with what would be expected by extrapolating the mass transfer rates observed in previous runs with other waters, for the case of a very large extraction factor. Thus, volatile-solvent extraction with isobutylene serves to remove the dissolved aromatics very effectively from this water.

The measured COD for the feed water is substantially less than would correspond to complete oxidation of the three aromatic species. This result is not surprising, in view of the fact that these aromatics are known to be refractory to both biological and chemical oxidation; hence the measured COD does not reflect the total amounts of dissolved organic species present. Similarly, the percentage removal of COD cannot be looked upon as a meaningful figure, except that it confirms that the decontamination of the water by isobutylene extraction is quite good. The refractiveness of the dissolved organics to oxidation is an incentive for treating the water by extraction, as opposed to biological oxidation, in practice.

Table 54. Results from Run RS19

Wastewater: Styrene Manufacture
Solvent: Isobutylene
Water Flow Rate = 3.00 gal/hr
Solvent Flow Rate = 0.543 gal/hr
Rotating Disc Diameter = 1.75 inch
Stator Hole Diameter = 2.00 inch
Rotational Speed = 1250 rpm

Analytical Results (concentrations in ppm)

Solute	Feed	Product	% Removal
Benzene	290	10	97
Ethylbenzene	120	4	97
Styrene	15	<1	>93

COD of Feed Water = 530 ppm
COD of Product Water = 50 ppm
% Removal of COD = 91%

SECTION IX

EFFECTS OF SCALE ON RDC DESIGN

The steps in the development of a new process usually include operation on one or more small scale units before a commercial process design can be developed. This is certainly the case for a waste water treatment process which is based on solvent extraction. In this chapter we consider how the data described in Section VIII for the RDC extractor can be used to project the design of a commercial process and to define the need for a pilot plant program. The extraction of phenol and MEK from a waste water using n-butyl acetate as solvent is used as an example, but the discussion also applies to other extraction processes.

Steps in Developing the Design of an RDC Extractor.

The initial step in developing the design of an RDC extractor would probably be done on as small a scale as possible. As an RDC is scaled down, mechanical factors limit the minimum size. The 3-inch diameter column used in this study is about as small as can be used to obtain valid data for scale-up. In a smaller unit the rotating shaft on which the discs are mounted would take up too large a fraction of the volume of the column. Even on the 3-inch RDC used in this study, it was necessary to install a bearing midway up the 4-foot long column to minimize shaft vibration. This bearing cut down the cross-sectional area available for fluid flow to the extent that a non-uniform hold-up was observed in some experimental runs.

Another factor affecting the operation of the RDC in this study was the volume of waste water which was available for testing. Since we found that about 45 minutes were required to reach steady operation, the 5-gallon samples we had available meant we had to use flow rates of 5 gal/hr or less. In a 3-inch RDC this flow produces a water-phase superficial velocity of 13.6 ft/hr, which is lower than what would usually be used commercially. Because the nature of this study was to investigate a variety of waste waters, we accepted these limitations and realized that further pilot plant study would be required to develop the commercial design.

A company with an existing or an anticipated process which produces a waste water stream that is amenable to treatment by solvent extraction would probably study the extraction step in a pilot plant. It would be desirable to use actual, fresh waste water either from an existing process or from a pilot plant. It would also be useful to operate the solvent regeneration equipment in a continuous manner to help fix the material balance for the entire extraction process. The problem of having a limited supply of waste water would not be as severe, so the pilot-scale RDC could be designed and operated in a manner that would give the best probability for successful scale-up to a full-scale plant.

Considerations in Changing Scale of an RDC.

In Section V the equations describing an RDC extractor were shown to suggest a rational basis for scale-up. This basis included holding the following quantities constant during a change in scale:

1) The ratios d_i/D, d_s/D, and H_c/D,
2) The superficial velocities, V_d and V_c, and
3) The power per unit mass, $\overline{P/M}$.

In addition consideration must be given to flooding tendencies and to axial mixing, both of which will change with changes in scale. We can use the results discussed in Section VIII to estimate the optimum values for these quantities on a commercial scale so that the pilot plant can be operated at the best possible set of conditions.

Consider as an example a waste water which contains phenol and MEK. The results in Section VIII showed that a good removal of phenol and a moderate removal of MEK could be achieved with a low solvent-to-water flow ratio ($F_s/F_w = 0.1$). We will consider a design for an RDC which operates with $F_s/F_w = 0.1$ using pure solvent feed and which achieves a 99% removal of phenol. We will consider such designs for two possible full-scale waste water flow rates, 10 gal/min and 100 gal/min. Within these constraints we will consider a partial optimization to define an RDC extractor of minimum cost. Note that to optimize the entire extraction process, the best value for F_s/F_w would also have to be determined as was done in Section IV for several processes. In this example we will consider only one value of F_s/F_w, so the cost of solvent regeneration will be fixed.

For the experiments with lube oil refining waste water, we found that the column hydrodynamics could be correlated by the equations of Strand, et al. (1962) using $G_{18} = 0.20$. Assuming a column temperature of 22°C leads to the physical properties listed in Table 55. The mass transfer estimates were made by assuming that N_w was equal to N_w from the turbulent mass transfer model divided by 0.5 and that N_s was equal to N_s from the stagnant drop model divided by 2.6; these ratios were determined from experimental data as described in Section VIII. The fraction of flooding was estimated by the method of Logsdail, et al. (1957).

The variables which were determined in the optimization were V_c and N (equivalent to optimizing $\overline{P/M}$). The ratios d_i/D, d_s/D, and H_c/D were held at the values used in the experimental RDC (i.e., $d_i/D = 0.5$, $d_s/D = 0.75$, and $H_c/D = 0.333$). The calculation procedure was as follows:

1. Assume a value for V_c. From the fixed F_s/F_w and F_w, calculate V_d and D.
2. Assume a value for the height of the column.
3. Calculate the removal efficiency for phenol as a function of the disc rotational speed, N. Locate the N corresponding to the

Table 55. Physical Properties for RDC Design Sample Calculation

Water-phase density = 0.9978 gm/cc

Water-phase viscosity = 0.955 cp

Solvent-phase density = 0.8788 gm/cc

Solvent-phase viscosity = 0.704 cp

Interfacial tension = 13.9 dyne/cm

Solute Diffusivities ($10^5 ft^2/hr$) in Water and in n-Butyl Acetate, and K_d's:

Solute	D_w	D_s	K_d
MEK	3.65	6.21	4.56
Phenol	3.47	6.04	57.0

greatest phenol removal, which at the same time corresponds to operating at 50% or less of the flooding velocities.

4. Iterate back to step 2 until a column height is determined which gives 99% phenol removal at the optimum value of N.
5. Repeat steps 1 to 4 for several values of V_c so that a plot of column height vs. D may be prepared.
6. Use the plot of D vs. column height to prepare a plot of column cost vs. V_c. Determine the value of V_c which gives the minimum cost.

These calculations were made using a CDC 6400 computer with the program RDC, which is listed in Appendix H.

This procedure will first be demonstrated for a waste water flow of 10 gal/min. Figure 28 is a plot of η (fraction of phenol not removed) vs. N for several values of V_c between 15 and 60 ft/hr. Consider the curve for $V_c = 15$ ft/hr. At 100 RPM the removal efficiency is about 80%. As N increases, the phenol removal improves because of better mass transfer. However, at about 265 RPM a minimum occurs, and at higher values of N axial mixing becomes more severe so that the removal efficiency drops. At 342 RPM the limit for 50% of flooding is reached. At larger values of N (dashed lines in Figure 28) the column is operating at greater than 50% of flooding. Since the minimum in the curve corresponds to 99% phenol removal, it is clear that the iteration between steps 2 and 4

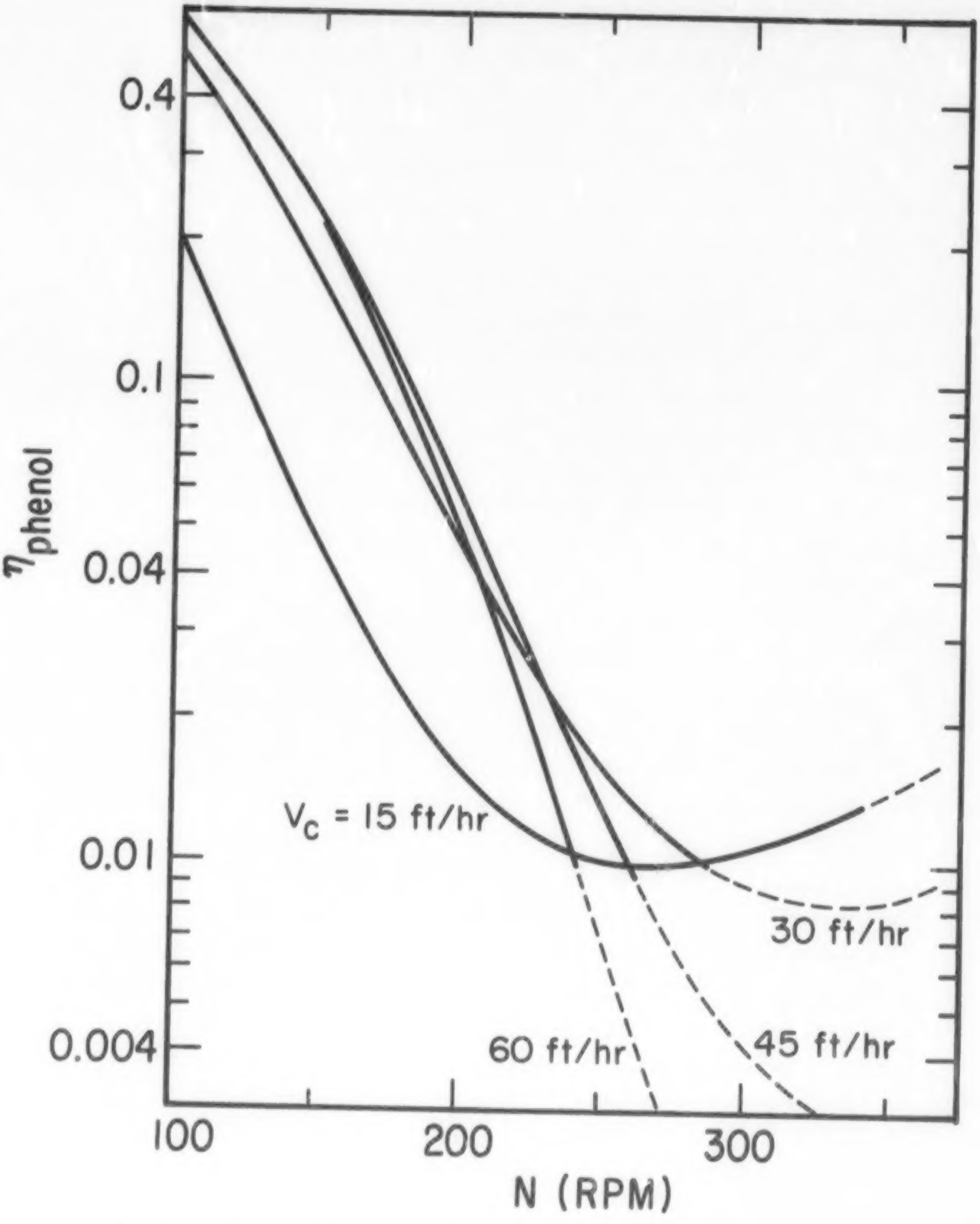


Figure 28. Effect of Rotational Speed on Phenol Removal at 10 GPM Waste Water Flow

above has already located the required column height (18.8 ft). Considering next the curves for larger values of V_c, we see that the constraint requiring the column to operate at or below 50% of flooding limits the maximum value of N before the minimum in the curve is reached.

Following the procedure in step 5 above, Figure 29 is a plot of D vs column height. All points on this curve correspond to 99% phenol removal at the optimum value of N. The curve in Figure 29 is used to determine the cost for a column using the cost data of Clerk (1964). His costs are for a fabricated RDC of carbon steel including discs, stator rings, manways, nozzles, supports, and skirt, but not including the motor. Clerk's data were updated to Dec. 1973 costs by using the Marshall and Stevens chemical equipment cost index. A plot of purchased cost vs. V_c is shown in Figure 30.

There are several points of interest on Figures 29 and 30. At high values of D in Figure 29 there is a region where increasing V_c tends to decrease both D and the column height. This result reflects the importance of axial mixing at low values of V_c. In this region the decrease in axial mixing is so significant that 99% phenol removal can be achieved in a shorter as well as smaller column when V_c is increased. In Figure 30 there is a minimum in the cost curve which occurs at a value of V_c of about 45 ft/hr. The cost for a column operating at V_c = 15 ft/hr is more than double the minimum cost.

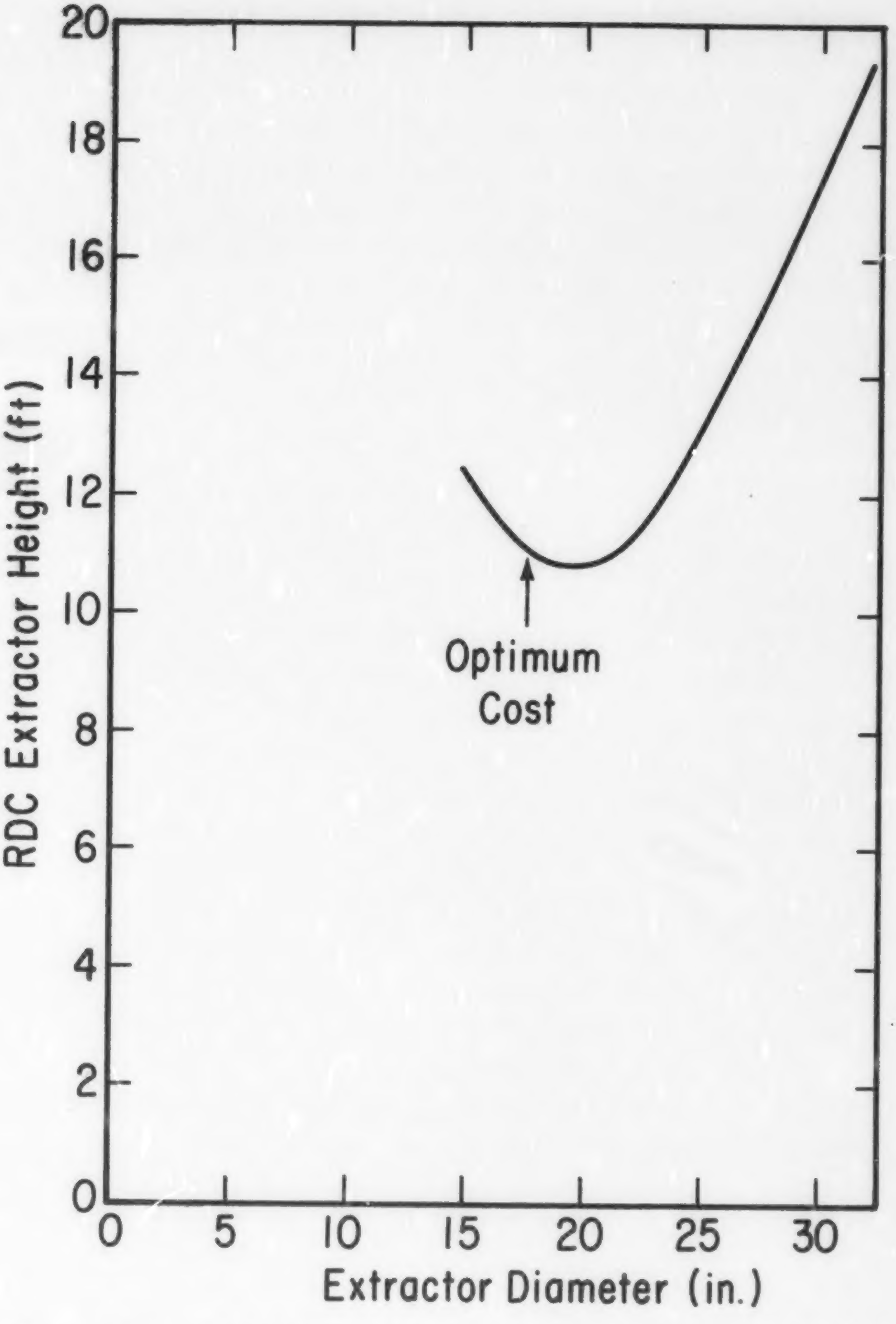


Figure 29. Extractor Size for 10 GPM Waste Water Flow

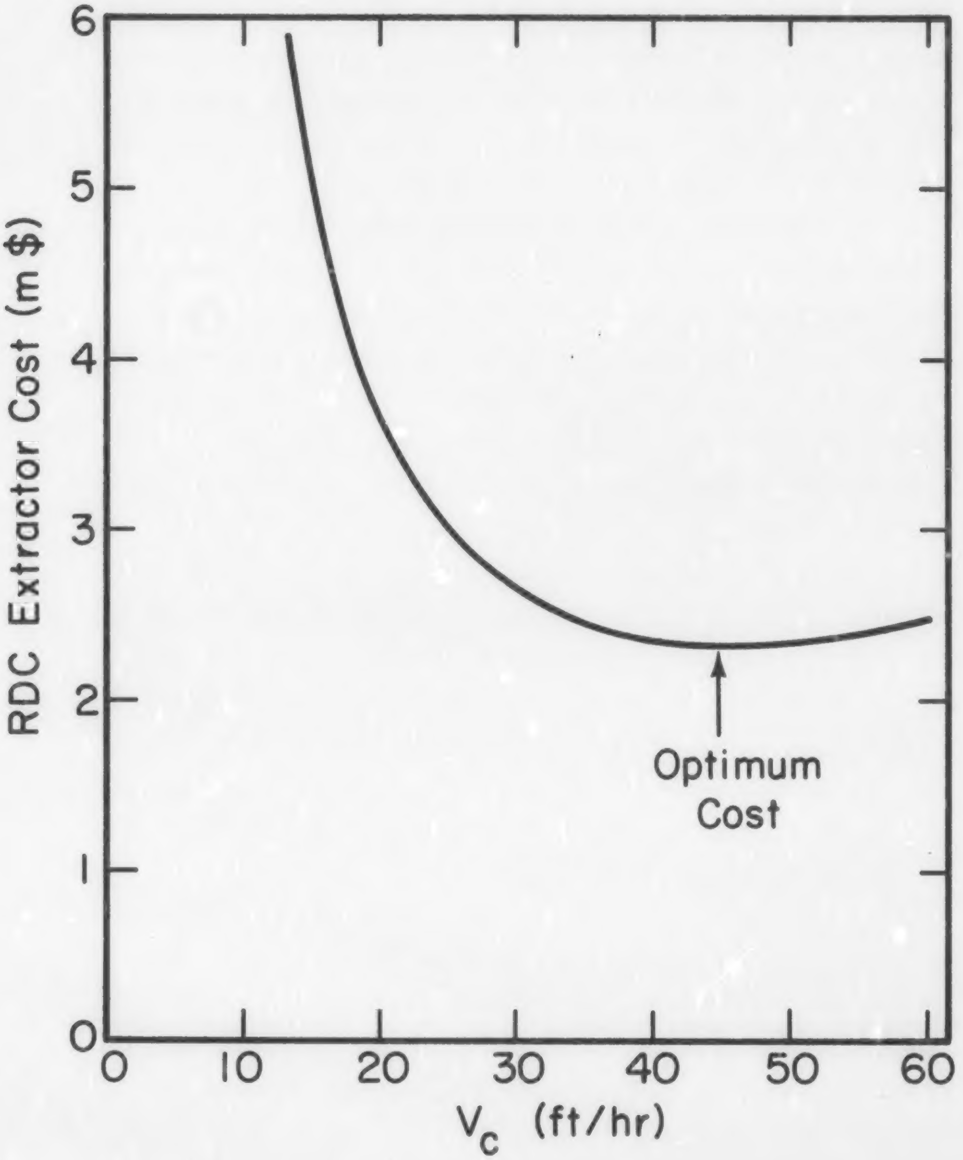


Figure 30. Extractor Cost for 10 GPM Waste Water Flow

The removal efficiency of MEK from this hypothetical waste water is only slightly affected over the range of column designs considered. For all cases when the removal efficiency for phenol was 99%, the removal efficiency for MEK varied between 40.6 and 43.4%. The removal efficiency at the optimum design for phenol removal was 43.3%.

A similar calculation was made for a waste water flow of 100 gal/min. Figure 31 is a plot of η vs. N for values of V_c between 15 and 90 ft/hr. Note that at this higher waste water flow rate, flooding begins to be the constraint limiting N at V_c of about 60 ft/hr instead of at 25 ft/hr as was found for 10 gal/min of waste water flow. Note also that the maximum removal efficiency occurs at a lower value of N in this larger column. Plots of column height vs D and cost vs V_c are shown in Figures 32 and 33. Some difficulty was encountered at the highest values of V_c for this case. At these conditions the differences between the flooding correlation of Logsdail, et al. (1957) and the correlation for V_k from Strand, et al. (1962) resulted in no solution being possible for 50% of flooding according to Logsdail, et al. A recent comparison of flooding correlations for an RDC (Landau and Houlihan, 1974) indicated the Logsdail, et al., approach was better when comparing data for small columns, but no comparison has been published for larger columns. Despite this problem at very high values of V_c, it is clear from Figure 33 that the optimum value of V_c is somewhat above 100 ft/hr.

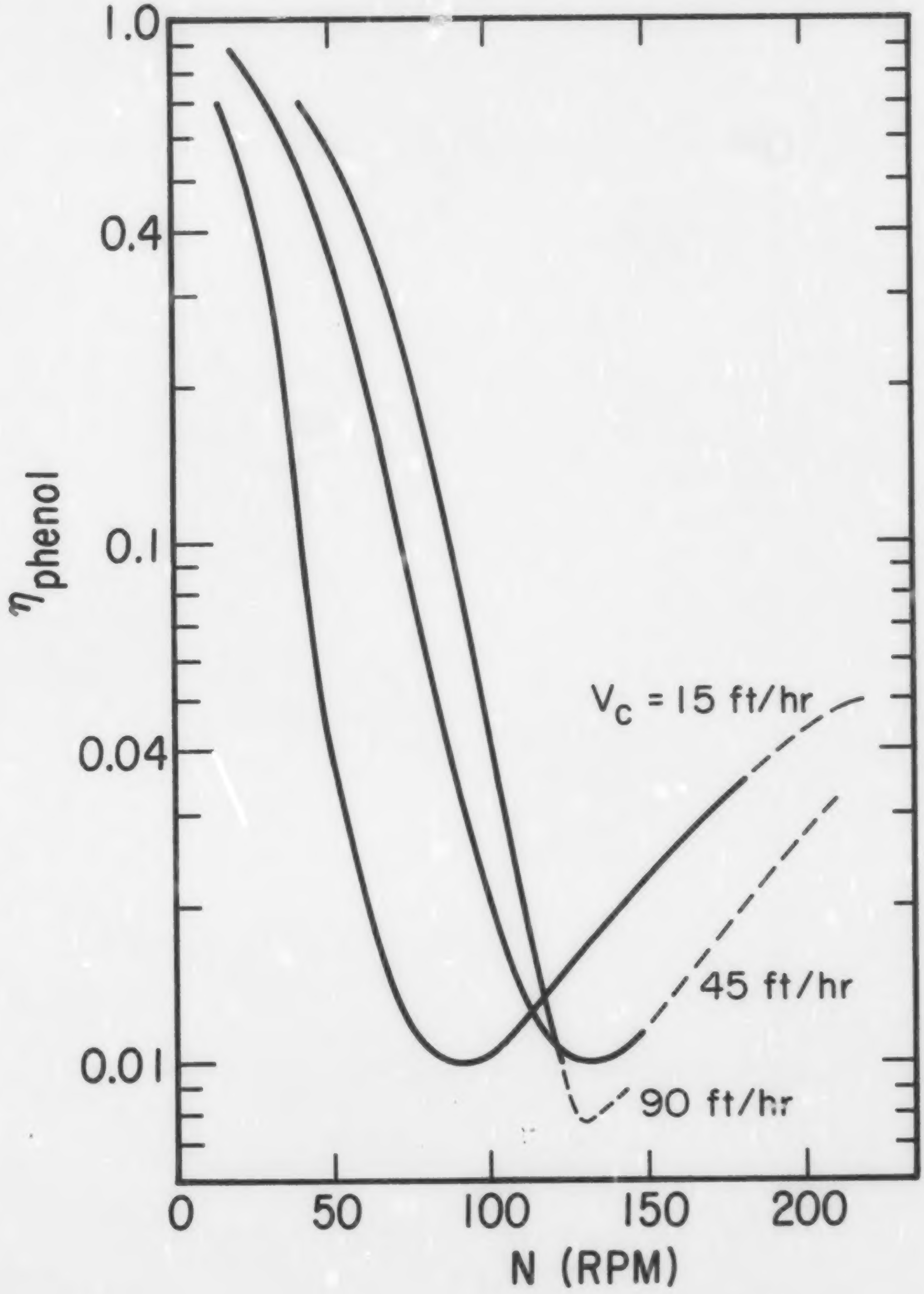


Figure 31. Effect of Rotational Speed on Phenol Removal at 100 GPM Waste Water Flow

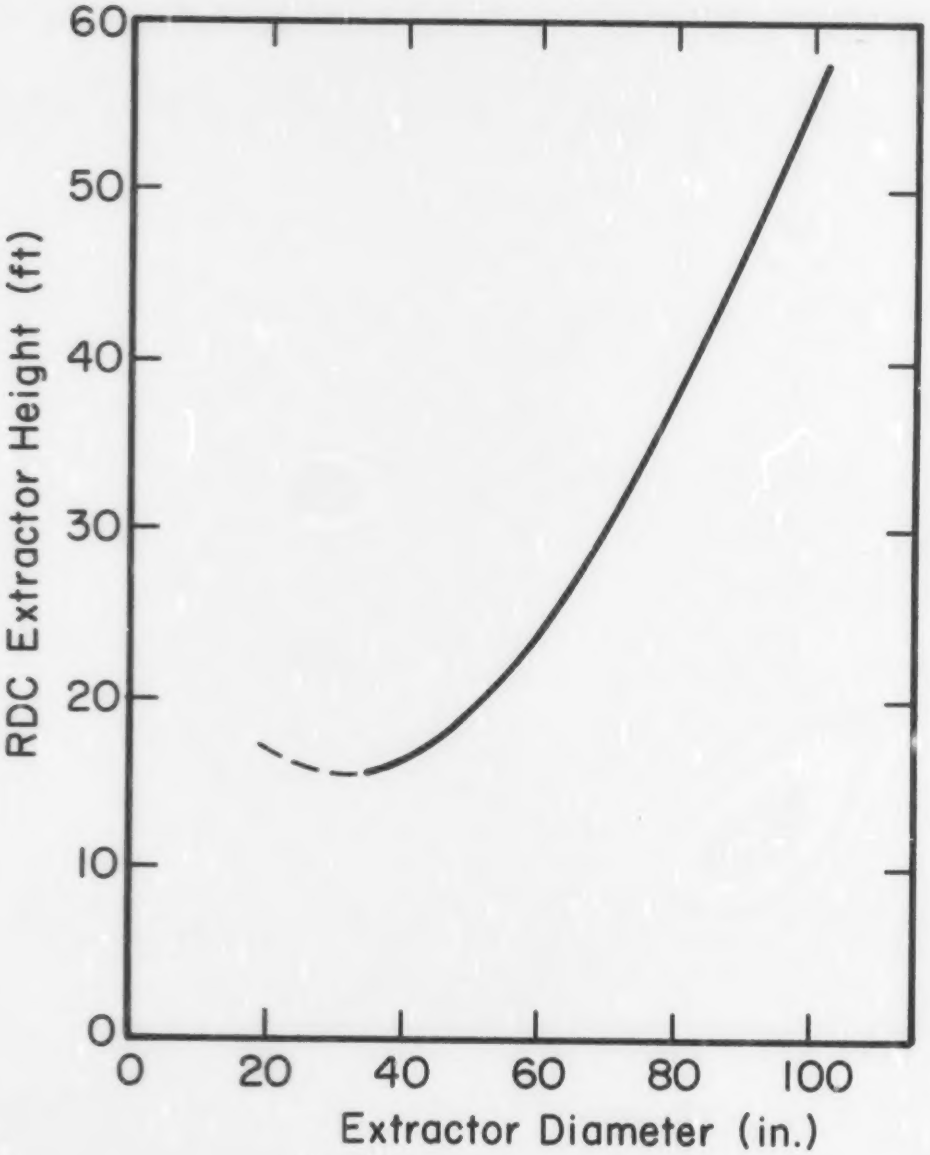


Figure 32. Extractor Size for 100 GPM Waste Water Flow

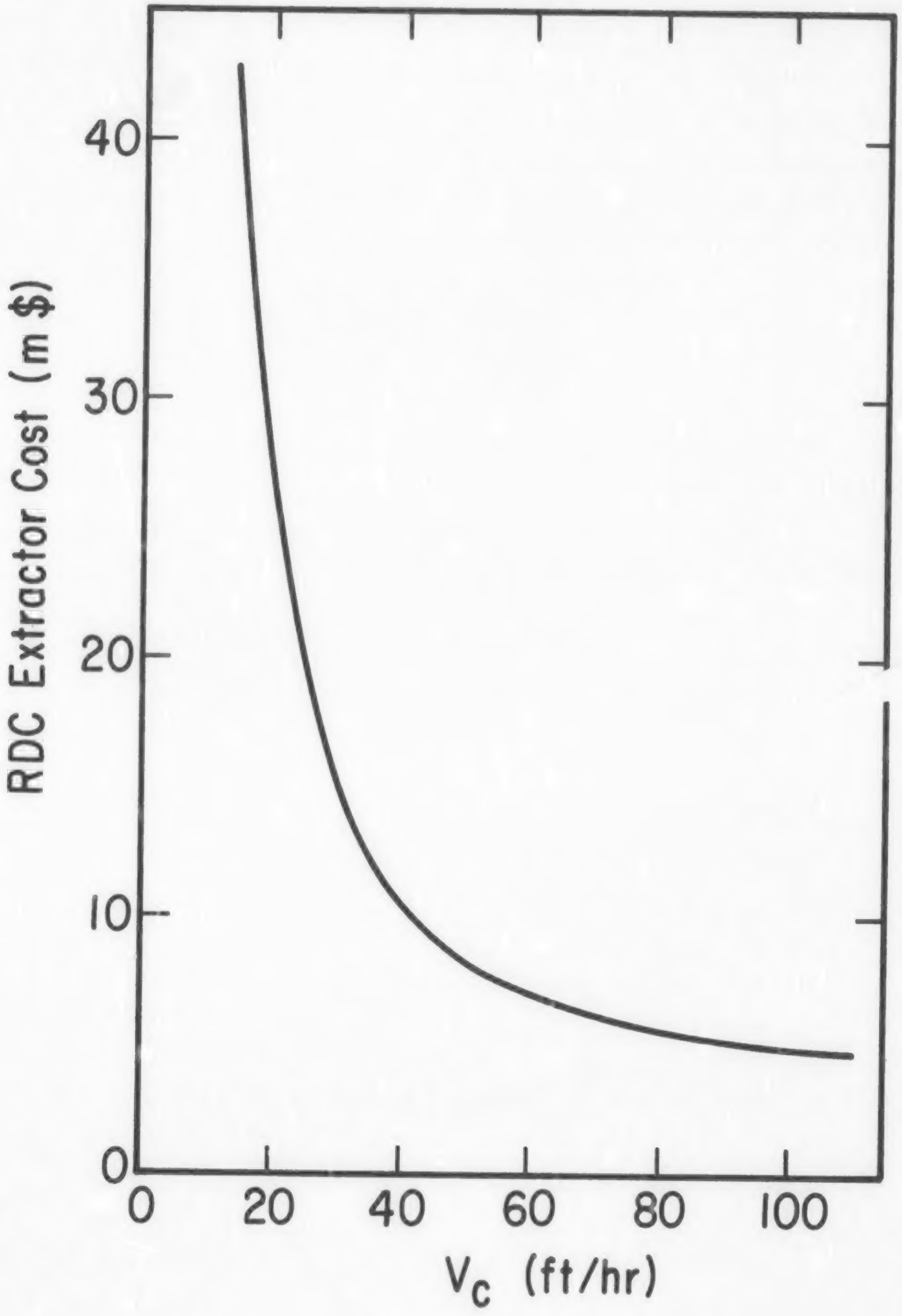


Figure 33. Extractor Cost for 100 GPM Waste Water Flow

Sizing a Pilot Plant RDC.

Once the optimum value of V_c has been determined, then a pilot plant RDC can be sized. Consider first a pilot scale RDC which will be used to gather data for the 10 gal/min waste water treatment. Assume that a 3-inch diameter column will be used. At the optimum value of V_c = 45 ft/hr, such an RDC would be able to treat 16.5 gal/hr or 0.275 gal/min of waste water. At the optimum operation of the large RDC, N = 260 RPM and $\overline{P/M}$ = 76.3 ft-lb_f/hr-lb_m. The 3-inch RDC would give the same $\overline{P/M}$ when N = 566 RPM.

The height of the pilot scale RDC can be chosen to achieve about the same removal efficiency as for the large extractor. A 3-inch diameter RDC operating at 566 RPM would have to be about 6.5 ft tall to give 99% phenol removal. The MEK removal would be about 44%. By choosing the pilot plant RDC in this manner, the loaded solvent composition would be about like that in the full-scale plant. This would make the operation of regeneration equipment very similar to the actual process.

The scale-up factor in terms of waste water flow rates from the 3-inch RDC to the 18-inch RDC would be about 36. A somewhat larger diameter pilot plant RDC might be chosen to reduce this scale-up factor. For the pilot plant RDC to be used to determine the design of the large RDC which would treat 100 gal/min, the diameter of the pilot plant would probably be larger. If a 6-inch diameter column were operated at V_c = 105 ft/hr, the pilot plant could process 2.57 gal/min giving a scale-up factor of 39.

At the optimum operation of the large RDC, N = 118 RPM and $\overline{P/M}$ = 28.0 ft-lb_f/hr-lb_m. The 6-inch column would give the same $\overline{P/M}$ at N = 316 RPM. However, this design would operate at 58.7% of flooding, so a slightly lower value of N might be used. At 316 RPM, the phenol removal efficiency for a 10-foot high column would be 99.2%, and the MEK removal would be 43.9%.

It should be noted that the calculations made in this chapter are only approximate. We have assumed that the ratio of theoretical to experimental mass transfer coefficients for each phase would remain constant over a wide range of operation. We also assumed that G_{18} would be constant. To compensate for these approximations, a pilot plant RDC should be designed with a variable-speed drive, and an experimental program should be designed which includes the investigation of a range of values for V_c. However, it is reassuring to note that the calculations predict RDC extractors of quite reasonable sizes (see Table 56).

Table 56. Summary of RDC Designs

For 10 gal/min full-scale flow

	Pilot Plant	Full-scale Plant
Waste Water Flow	0.275 gal/min	10 gal/min
Column Diameter	3 inches	18 inches
Column Height	6.5 ft.	10.9 ft.
Rotational Speed	566 RPM	260 RPM

For 100 gal/min full-scale flow

	Pilot Plant	Full-scale Plant
Waste Water Flow	2.57 gal/min	100 gal/min
Column Diameter	6 inches	38 inches
Column Height	10 ft.	15.8 ft.
Rotational Speed	316 RPM	118 RPM

SECTION X

SUMMARY AND DISCUSSION OF APPLICATION

In previous Sections we have discussed general process considerations relative to treating a waste water for the recovery of chemical pollutants and have described an experimental program in which solvent extraction was studied in a small pilot plant. We studied a variety of potential and actual pollutants with a major portion of the program being directed toward the use of a volatile solvent. In experiments conducted using an RDC extractor, we also demonstrated several promising extraction process configurations which utilize a less-volatile, polar solvent as well as a volatile solvent.

In this chapter we will extend the experience gained from the general process considerations and from the experimental study to develop a strategy for choosing a processing technique for a waste water generated by the petroleum, petrochemical, or organic chemical industry. Any particular waste water stream will have its own characteristics which will probably require further research and process development, but the strategy to be described should be useful in directing such further study in the most promising direction.

Strategy of Process Selection.

The initial step in choosing a promising processing method is to quantify the major pollutants present in the waste water. We will direct our attention primarily to individual waste water streams which do not contain more than a few major pollutants. The analytical techniques based on gas chromatography (Herz, 1972; Sugar and Conway, 1968) should be most useful in identifying the pollutants. Gas chromatography may also be among the most attractive methods for quantitative analysis. If the waste water stream comes from an existing plant, then a sampling program should be able to determine the typical range of concentrations for the major pollutants. In the development of a new process, the determination of typical concentrations of pollutants in anticipated waste water streams should be a part of the process development.

The next step is to determine the value of the pollutants. The value of the individual pollutants can be estimated by assuming a substantial fraction recovery and sale at a price of approximately one-half to one times the present market value. When several pollutants are present, the value of the mixture should also be estimated. If this mixture can be recycled to the process, its value can be estimated from the reduction in raw material needs or the increase in product yield. When considering recycle it is important to realize that all pollutants will be recycled so that the product quality may be affected. The pollutant value can be determined in units of $/thousand gallons of waste water.

The next step is to decide if recovery is promising. If the value of pollutants is greater than about $3/thousand gallons, then recovery for pollutant value is a promising possibility. If the value is between $1 and $3/thousand gallons, then the possibility of recovery should be considered. If the value of pollutants is below $1/thousand gallons, then recovery will seldom be economically justified. When a non-recovery technique is indicated, biological oxidation or carbon adsorption are likely techniques.

In cases where one or more of the major pollutants is refractory to treatment by biological oxidation or is toxic to the bacteria, then a process which concentrates these pollutants may be the best approach even though the pollutant value is below $1/thousand gallons of waste water. Solvent extraction, particularly with a volatile solvent, should be considered as an alternative waste water treatment technique. The strategy for choosing between solvent extraction and steam stripping as a method for generating a concentrated pollutant stream is the same as that described below for the case of a recovery technique. The best solvent extraction or steam stripping process can then be compared to carbon adsorption.

When the pollutant value indicates that a recovery process is promising, steam stripping and solvent extraction should be the principal approaches considered. In rare cases, other recovery processes such as carbon adsorption or reverse osmosis could be considered, but these techniques will generally be more expensive than either steam stripping or solvent extraction. Although we refer to the process as steam stripping, reflux will be required to produce an organic product with a low water content. The process is actually distillation.

The next step is to choose a good solvent extraction process so that the comparison between extraction and stripping is valid. The determination of a steam stripping process arrangement will not be developed here, except to note several factors which make steam stripping less favorable. The lower the relative volatility of the organic pollutant, the more difficult it is to remove by stripping. Since with all but the lowest molecular weight organic compounds an azeotrope will occur at some concentration, the lower the organic content in the azeotrope, the less highly purified is the recovered pollutant stream from a steam stripping process. With the higher molecular weight organic compounds, a heterogeneous azeotrope will form. There is an advantage in terms of the ease of separation when the distillate separates into two phases as it is condensed. When the waste water is corrosive, steam stripping at elevated temperatures will aggravate the problem, while solvent extraction at ambient temperature will be favored.

In trying to identify a good solvent extraction process, first consider volatile solvent extraction. A value of K_d for each pollutant distributing between isobutylene or isobutane and water should be estimated. The data of Appendix E will be useful in making this estimate. A simple experimental extraction at atmospheric pressure using pentane or hexane may also be useful in estimating K_d. If K_d is greater than about 10, then volatile solvent extraction should be a good choice. If K_d is between 2 and 10, volatile solvent extraction may still be useful, but other feasible techniques should also be considered. If K_d is much less than 2, then volatile solvent extraction will probably be uneconomical.

When a mixture of pollutants is present, all pollutants which are extracted will be recovered as a single mixture when using volatile solvent extraction. Separation of this mixture into its components may be a practical consideration. When the pollutants have a range of values of K_d, then it may be desirable to extract only those components with high values of K_d. The components with low values of K_d may not be worth recovering, or another recovery method might be considered.

If the value of K_d between water and isobutylene or isobutane is low, then consider dual solvent extraction. Values for K_d for each pollutant distributing between water and a polar solvent should be estimated. The polar solvents best suited for the dual solvent process generally are those having a water solubility between 0.5 and 2.0%. Some examples are n-butyl acetate, methyl isobutyl ketone, n-hexanol, diisopropyl ether, and ethylene dichloride. The data reported here or K_d data from other sources may be used in some cases, and experimental estimates for K_d may be made fairly simply in other cases. A variety of polar solvents should be tested since some pollutants may be very readily extracted by one polar solvent and not well extracted by others (e.g. chloral). By choosing polar solvents with the above range of water solubilities, there is a good chance that K_d for the polar solvent distributing between water and a volatile solvent will be high. Mixtures of polar solvents may also be considered.

Once the polar solvent is identified which gives the highest value of K_d of those considered, this value of K_d should be compared with the value of K_d for volatile solvent extraction. If the value of K_d for polar solvent extraction is no more than about a factor of 2 higher than the value of K_d for volatile solvent extraction, then the dual solvent process will not hold an advantage over volatile solvent extraction. The data in Appendix E for aliphatic aldehydes indicate that this class of organic compounds have values of K_d for isobutylene extraction which are only slightly less than for many polar solvents. Typically dual solvent extraction will be favored over volatile solvent extraction when the values for K_d in both dual solvent extraction steps are larger than 20 while the value for K_d for volatile solvent extraction is less than about 5. This is the case for phenol extraction since for extraction by n-butyl acetate K_d = 57.0 and for n-butyl acetate recovery by isobutylene K_d = 168, while K_d = 0.70 for extraction of phenol using isobutylene.

When a mixture of pollutants is present, then the relative volatility between the polar solvent and each pollutant must be considered when the polar solvent will be regenerated by distillation. If the polar solvent is more volatile than all pollutants or less volatile than all pollutants, then a single mixture of pollutants will be produced with a dual solvent process. However, if some pollutants are more volatile than the polar solvent and others are less volatile, then an additional distillation would be required to regenerate the polar solvent. It is much less likely that a dual solvent process with an additional distillation step necessitated by relative volatility considerations would be less expensive than some other recovery technique.

The use of a polar solvent extraction step for the removal of certain pollutants does not necessarily dictate the use of volatile solvent extraction for the recovery of the dissolved polar solvent. It would be possible to use steam or inert gas stripping (as in the Phenosolvan process described in Section III) for polar solvent recovery. However, when the polar solvent is chosen from solvents having a water solubility of 0.5 to 2.0 weight %, then it is likely that volatile solvent extraction will be a good choice. In Section IV we suggested two flow scheme variations for a dual solvent process. When the dual solvent process with linked solvent cycles has advantages over the dual solvent process with separate solvent cycles, then volatile solvent extraction rather than a stripping technique would have to be used for polar solvent recovery to accrue these advantages.

We are not yet able to make many quantitative generalizations on which of the two dual solvent process arrangements would be best. However, when the polar solvent is more dense than water (e.g., ethylene dichloride), a dual solvent process with linked solvent cycles would probably not be used because this would decrease the density difference between mixed solvent and water. When the polar solvent is slightly less dense than water and the presence of the pollutant decreases this density difference (e.g., extraction of phenol with n-butyl acetate), then a dual solvent process with linked solvent cycles will tend to be favored.

The final step is to compare the best solvent extraction process with steam stripping. In Section IV this comparison was made for the recovery of n-butyl acetate using either steam stripping or volatile solvent extraction with isobutylene. This solute has properties which favor both steam stripping (by forming a heterogeneous azeotrope) and volatile solvent extraction (a large K_d of 168). When costs were compared for these processes they were essentially equal, even though the assumptions made with respect to the distillation column stage efficiency were shown to favor the steam stripping process. It is reasonable to expect that economic considerations will favor volatile solvent extraction in many cases.

The comparison between the cost of pollutant recovery by steam stripping and the cost of pollutant recovery by dual solvent extraction is expected to favor steam stripping in the majority of cases. The reason why dual solvent extraction is favored in some cases is apparent when details of steam stripping processes are considered. The concentration of organic in the liquid phase for a homogeneous azeotrope or in the organic-liquid phase for a heterogeneous azeotrope determines the maximum purity of the recovered organic solute. For phenol, the azeotrope contains only 9 weight % phenol (all these quoted azeotropic concentrations are from Weast, 1970). For acetic acid, the azeotrope contains only 3 weight % organic. It is interesting to note that these two solutes are often recovered by solvent extraction. Many alcohols also show fairly low organic contents in their water azeotropes. For example, azeotropic mixtures with n-propanol, n-butanol, cyclohexanol, and benzyl alcohol contain 72, 56, 20, and 9 weight % organic, respectively. However, these alcohols tend to have higher relative volatilities with respect to water than does phenol or acetic acid. This makes it easier to reach the azeotropic composition and easier to produce purified water. Organic acids and amines are other classes of organics which form water azeotropes which have low organic contents. Other specific organics which show this property include furfural and pyridine.

The above discussion has been directed toward pollutants which are soluble in water. When dispersed organics are present, steam stripping is probably not the best alternative to be compared with volatile solvent extraction. Mechanical separation techniques, such as using a coalescer or a centrifuge, are likely ways to separate the dispersed organics. However, if an appreciable quantity of dissolved organics is also present, then solvent extraction has the advantage of being able to remove both dispersed and dissolved pollutants in one step. Simply centrifuging a sample of the waste water and measuring the remaining organic content would determine if a treatment for dissolved pollutants is necessary. Solvent extraction using a volatile solvent is expected to be an economical approach to recovering a dispersed organic pollutant in a number of cases.

Examples Illustrating the Strategy of Process Selection.

Consider a waste water which has been determined to contain 2 weight % methanol as the major pollutant. The pollutant value of about $3/thousand gallons of water makes recovery a promising approach. Based on the trends of K_d with decreasing molecular weight for alcohols, neither volatile nor dual solvent extraction is promising. Since methanol does not form an azeotrope with water and is considerably more volatile than water, steam stripping would be preferred.

Consider a waste water which has been determined to contain 0.1 weight % crotonaldehyde. The pollutant value if recycled to an n-butanol plant is about $1/thousand gallons (based on full market price of butanol). Although the pollutant value is fairly low, at this concentration crotonaldehyde is a bacteriacide which makes biological oxidation difficult. Recovery is presently accomplished by steam stripping; however, recovery by volatile solvent extraction may be a promising alternative. The value of K_d between water and isobutylene is 2.48 (Appendix E), and the value of K_d for the best polar solvent, octanol, is estimated to be about 8. With this little difference in K_d for the volatile solvent and K_d for the polar solvent, it is likely that the volatile solvent extraction process would be favored, unless there are other major pollutants present which could only be extracted with a polar solvent.

Consider the lube oil refining waste water which contained 2 weight % phenol, 0.2 weight % o-cresol, and about 0.02 weight % MEK. The value of phenol and o-cresol is about $17/thousand gallons (based on full market value since they could be recycled to the lube oil treating system). The value of the MEK is only $0.2/thousand gallons. This is a case where we might consider recovering only phenol and o-cresol and treating the MEK by biological oxidation. With steam stripping all three components would be recovered as a single mixture; the difficulty of obtaining a phenol product of low water content in such a case has been discussed above. The value of K_d for phenol using isobutylene is only 0.7, so volatile solvent extraction would not be economical. However, using n-butyl acetate as the polar solvent in a dual solvent process would be an effective method of recovering only phenol and o-cresol. Since the volatility of MEK is greater than that of n-butyl acetate, it would not be separated during polar solvent regeneration. MEK would build up to a steady-state level in both recirculating solvents. This equilibrium level would be less than 0.1 weight % in each solvent, so that the presence of MEK should not affect the extraction of the phenolics.

Finally consider the ethylene quench waste water. The concentrations of the major identified pollutants (benzene, toluene, xylenes, and phenol) are all below 0.01%. Their economic value is much less than $1/thousand gallons, but all except phenol are refractory to biological oxidation. There is also a considerable amount of dispersed organics present. Steam stripping would probably produce a distillate which contains a dispersion of organic droplets. Tests in the pilot plant showed that volatile solvent extraction using isobutane removed both the dispersed and the dissolved organics. This would probably be the best method of recovery, although this step might just be used to concentrate the organic pollutants for another disposal method.

SECTION XI
NOMENCLATURE

Symbol	Definition	Units
A	Cross-sectional area of column	ft^2
A_p	Surface area of fully formed drop	ft^2
a	Interfacial area per volume in column	ft^2/ft^3
C_R	Area ratio - see Equation (B14)	
D	Column diameter	ft
D_d, D_c	Solute diffusivity - see subscripts below	ft^2/hr
d_i	RDC disc diameter	ft
d_s	RDC stator hole diameter	ft
d_p	Drop diameter	ft
E	Extraction factor (= K_d F_s/F_w)	
F	Mass transfer parameter - see Appendix B	
F_s, F_w	Flow rate - see subscripts below	lb/hr
G	Constant	
g_c	Conversion factor (4.18 x 10^8)	lb_m-ft/ lb_f-hr^2
H	Overall column height	ft
H_c	RDC compartment height	ft
h	Distance variable - Appendices B & C	ft

K_d	Distribution coefficient (by weight)	
K_d^{∞}	Distribution coefficient at infinite dilution	
K_d^{mix}	Distribution coefficient with mixed solvent	
K_{ow} (K_{oc})	Overall mass transfer coefficient based on water (or continuous) phase concentrations	ft/hr
K_{df}	Overall mass transfer coefficient to drop during its formation based on drop phase concentration	ft/hr
k_d, k_c	Individual-phase mass transfer coefficient - see subscripts below	ft/hr
MW_i	Molecular weight of i	lb/lb mol
m	Defined in Equation (B8)	
N	RDC rotational speed	RPM
N_w, N_s	Individual-phase number of transfer units - see subscripts below	
N_{ow}	Overall number of transfer units based on water phase concentrations	
P	RDC power input per compartment	ft-lb_f/hr
Pe_d, Pe_c	Peclet number based on column height - see subscripts below	
Pe*	Local Peclet number	
Po	Power number - see Equation (B9)	
$\overline{P/M}$	Power per unit mass - see Equation (B11)	ft-lb_f/ hr-lb_m
Q	Ratio of experimental N_{ow} to theoretical N_{ow}	
q_i	Roots of Equation C12	

R	Mass transfer parameter - see Appendix B	
RDC	Rotating Disc Contactor	
Re	RDC disc Reynold's number	
V_c, V_d	Superficial velocity - see subscripts below	ft/hr
V_k	Characteristic velocity - see Equation (B1)	ft/hr
V_n	Characteristic velocity - see Equation (B16)	ft/hr
V_s	Slip velocity - see Equation (B1)	ft/hr
V_t	Drop terminal velocity	ft/hr
V_{cf}, V_{df}	Superficial velocity at flooding - see subscripts below	ft/hr
W	Coalescence coefficient - see Equation (B16)	
X	Solute weight ratio in water phase	
X*	Equilibrium solute weight ratio based on water phase (= Y/K_d)	
X^i	Solute weight ratio at the interface	
X_{in}	Solute weight ratio in inlet water	
X_{wo}	Solute weight fraction in outlet water	
X_{wi}	Solute weight fraction in inlet water	
X_{si}	Solute weight fraction in inlet solvent	
Y	Solute weight ratio in solvent phase	

Y^i	Solute weight ratio at the interface	
Y_{in}	Solute weight ratio in inlet solvent	
Z	Dimensionless variable (= h/H)	
ε_w, ε_s	Axial dispersivity - see subscripts below	ft^2/hr
$\gamma_i^{(j)}$	Activity coefficient of component i in phase j	
μ_c, μ_d	Viscosity - see subscripts below	lb/ft hr
η	Dimensionless concentration - see Equation (1)	
ϕ	Fractional hold-up of dispersed phase	
ϕ_f	Fractional hold-up at flooding	
ρ_c, ρ_d	Density - see subscripts below	lb/ft^3
σ	Interfacial tension	lb/hr^2
θ_f	Time for drop formation - see Equation (B7)	hr

Subscripts	Meaning
c	Continuous phase
d	Dispersed phase (except K_d)
w	Water phase
s	Solvent phase

SECTION XII

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Section XIII

Publications

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APPENDIX A
BASIS FOR COST ESTIMATES

The estimates of investment and operating costs included in this report have been completed on a consistent basis. This consistency allows a valid comparison of alternatives (e.g., steam stripping and solvent extraction), but the absolute value of costs can only be compared with quoted costs from other sources when the estimating methods of the other authors are also clearly recorded. The method used herein makes extensive use of the capital cost estimating methods of Guthrie (1969) and the operating cost estimates of Peters and Timmerhaus (1968). To include the effect of inflation, all costs are corrected to December, 1973, by using the Marshall & Stevens chemical process industry cost index. Precision is ± 30%.

Estimated Total Plant Investment

To estimate the capital cost of an installed plant, the "module" technique of Guthrie was used. A set of assumptions (listed in the text) was established which allowed the heat and material balances to be determined. On the basis of a second set of assumptions (in lieu of a detailed optimization), the major pieces of on-site equipment (extraction and distillation columns, heat exchangers, tanks, pumps, etc.) were sized to perform the necessary stream transformations. Then the cost diagrams of Guthrie were used to determine the cost of each major item of equipment. All equipment was assumed to be constructed of carbon steel, but a 10% increase in cost was arbitrarily added for equipment which would be in contact with the waste water to accourt for slightly more severe corrosion. For items of equipment whose cost was not given by Guthrie, cost data from other sources were used and were treated to make them as consistent with Guthrie as possible.

Guthrie gives factors for each type of equipment which when multiplied by the cost of the item of equipment provides estimates for the auxiliary equipment (piping, concrete, instruments, etc.) cost, the labor costs for material erection and equipment installation, and the indirect (freight, construction overhead, engineering, etc.) costs. Typical total factors range from 3.29 to 4.23 for process equipment. The resulting installed equipment cost was then increased by 18% for contingency plus contractor's fee. No costs were included for site development or industrial buildings. The off-site investment for steam capacity, power generation, and cooling tower facilities (Guthrie, 1969) was found to be negligible for the cases considered. The working capital, which would include solvent and recovered pollutant inventories, was assumed to be negligible.

In the text, the total of the above costs is listed as the "Total Plant Investment." The percentage of this total which is associated with each item of on-site or off-site installed equipment is also listed. The details of individual pieces of equipment are discussed only in unusual situations.

Annual Operating Costs

The plant is assumed to operate for 8000 hours/year. The following items are included in the operating costs (Peters and Timmerhaus, 1968):

1. Chemicals - cost of solvent to make up for losses in the product water and in the recovered pollutant was included at the market price of the solvent.
2. Utilities - cost of steam, cooling water, and electricity were estimated by increasing the prices given by Peters and Timmerhaus by 3% per year for inflation. The following values were used:

Steam:	Exhaust	$0.40/1000 lb.
	100 psig	$0.80/1000 lb.
Cooling Water		$0.05/1000 gal.
Electricity		$0.02/kw-hr.

3. Maintenance and Repairs - annual cost was taken as 6% of Total Plant Investment.
4. Operating Supplies - annual cost was taken as 15% of Maintenance and Repairs.
5. Depreciation - annual cost was taken as 8% of Total Plant Investment.
6. Insurance and Taxes - annual cost was taken as 3% of Total Plant Investment.

7. Return on Investment - cost was assumed to be 8% of Total Plant Investment.

The above costs can be summarized in a single equation as follows:

Annual Operating Costs = Chemicals + Utilities
+ 0.259 (Total Plant Investment).

In addition to these operating costs, five more items associated with operating labor and laboratory charges should be listed (Peters and Timmerhaus, 1968). These five items are not included in the costs reported in this dissertation, not because they are unimportant, but because an accurate method of estimating them is not apparent. To estimate labor costs, manpower requirements must be estimated, and these vary greatly from company to company. Bollen (1974) suggests that 1/4 shift would probably be sufficient to operate this type of waste treatment process. To estimate laboratory charges, the types of waste water analyses, their cost, and their frequency must be estimated. An arbitrary cost of $1.00/hr seems reasonable. Based on these estimates, the additional five items would be as follows:

8. Operating Labor - cost assumed to be for one-fourth man at $4.00/hr. to give a constant value of $8,000/year.
9. Supervisory and Clerical Labor -cost was taken as 15% of operating labor.
10. Plant Overhead - cost was taken as 60% of Operating, Supervisory and Clerical Labor.

11. Administration - cost was taken as 50% of Operating Labor.
12. Laboratory - assumed to be $1.00/hr. mainly for analyses to give a constant $8,000/year.

If included, these items would result in an additional annual cost of $26,700, or for a 100 GPM waste water stream, $0.56 per thousand gallons treated. This is certainly an appreciable additional cost.

In the text, the total operating cost is listed usually as a value per thousand gallons of waste water treated. The individual costs are also listed for chemicals, utilities, and capital equipment costs (Items 3, 4, 5, 6 and 7).

APPENDIX B

HYDRODYNAMICS, AXIAL MIXING AND MASS TRANSFER IN CONTINUOUS EXTRACTORS

Spray column extractors.

For spray column extractors, the design procedure which was recommended by Treybal (1973) appears to be the best available in terms of hydrodynamics and mass transfer rates. Treybal's recommendation relies substantially on the article by Hughmark (1967). Several recent articles which concern axial mixing in spray column extractors were not included in Treybal's review, and these are discussed below. Most of the equations appear in Treybal's review (1973), and many of them are not repeated here.

The hydrodynamics of a spray column extractor is largely determined by the means of generating dispersed-phase droplets. The materials of construction must be chosen so that the distributor plate is preferentially wet by the continuous phase when a flat plate with holes drilled through it is to be used. For dispersing an organic phase into water, stainless steel can be used; for dispersing water into a continuous organic phase, a plastic distributor should operate well. When this precaution is taken, the correlation of Scheele and Meister (1968) permits the calculation of drop volume for cases when the velocity of dispersed phase flowing through the drilled holes is less than the jetting velocity. The droplet diameter may then be calculated by assuming that the droplets are spherical. Use of this correlation requires data on the interfacial tension between solvent and water, the density of both phases, and the viscosity of the continuous phase, as well as a choice of orifice diameter and the discharge velocity. The correlation was developed using pure fluid phases, so the effect of simultaneous mass transfer is unknown (Treybal, 1973). The error introduced by using pure-phase properties will be most serious when the water-phase is dispersed at the end of the column where pollutant concentrations are highest.

For the purpose of developing a design procedure for describing flooding and hold-up, it is useful to define a slip velocity, V_s, and a characteristic velocity, V_k, as follows (now using terminology of continuous-phase and dispersed-phase rather than solvent-phase and water-phase since the equations apply for either phase being dispersed):

$$V_s = V_k (1 - \phi) = \frac{V_d}{\phi} + \frac{V_c}{1 - \phi} \qquad \text{(B1)}$$

where ϕ = dispersed phase (fractional) hold-up. Thornton (1956) found that V_k was practically constant at conditions near flooding and assumed that if V_c is held constant and V_d is increased by increasing ϕ, then $\partial V_d/\partial\phi = 0$ at the flooding point (Thornton and Pratt, 1953). Solving the second equality in equation (B1) for V_d and setting the partial derivative to zero leads to the following three equations (subscript f refers to the flooding point):

$$V_{cf} = V_k \, (1 - 2\,\phi_f)\,(1 - \phi_f)^2 \qquad \text{(B2)}$$

$$V_{df} = 2V_k \phi_f^{\,2}\,(1 - \phi_f) \qquad \text{(B3)}$$

$$\phi_f = \frac{[(V_{df}/V_{cf})^2 + 8[V_{df}/V_{cf}]^{\frac{1}{2}} - 3\,V_{df}/V_{cf}}{4(1 - V_{df}/V_{cf})} \qquad \text{(B4)}$$

Equation (B4) implies that the hold-up at the flooding point is a unique function of the ratio of phase velocities and is independent of drop size and liquid physical properties. A correlation of V_k as a function of physical properties and drop size then will provide a method of estimating flooding. Treybal (1973) recommends the correlation of Minard and Johnson (1952) as providing the best estimate of the effect of phase densities, continuous-phase viscosity, and droplet diameter on V_{cf}; he also recommends that velocities no larger than 40% of V_{cf} be used.

For an estimate of the mass transfer rate, it is necessary to estimate the interfacial area per unit volume of contactor, a. For spherical drops, a is related to hold-up and droplet diameter, d_p, by the following:

$$a = \frac{6\phi}{d_p} \qquad \text{(B5)}$$

To calculate a, it is necessary to estimate ϕ at conditions well below the flooding velocities. If V_k were constant over a wide range of ϕ, then equation (B1) could be used. However, Treybal (1973) recommends using a method developed by several authors (Beyaert, et al., 1961; Weaver, et al., 1959) which is based on the finding that the ratio of slip velocity, V_s, to the terminal velocity of a single particle or droplet through a quiet fluid, V_t, is a unique function of the hold-up for all gas-solid, liquid-solid, and liquid-liquid systems. This allows the correlation of Zenz (1957) for the fluidization of solids to be used to predict hold-up in liquid-liquid systems since a correlation is available for predicting the terminal velocity of a liquid droplet (Klee and Treybal, 1956). Hughmark (1967) presents an equivalent method which is slightly easier to use.

Although the importance of axial mixing in solvent extraction was first noted following measurements of the continuous-phase concentration profile in a spray column (Geankoplis and Hixon, 1950), there have been few quantitative studies of axial dispersion in this type of contactor. For this reason Treybal (1963), basing his considerations on experimental measurements of continuous- and dispersed-phase concentration profiles (Cavers and Ewanchyna, 1957; Gier and Hougen, 1953), suggested that the continuous phase be considered as completely mixed ($Pe_c = 0$) and that the dispersed phase be considered to move in plug flow ($Pe_d = \infty$). For normal operation, the $Pe_d = \infty$ assumption still appears to be valid, but the experimental work of Brutvan (1958), Hazlebeck and Geankoplis (1963), and Henton and Cavers (1970) provides a basis for making a better approximation of the value of Pe_c.

The fact that the continuous phase often behaves as though it were completely mixed is the main reason spray columns are seldom used commercially. Only in cases where no more than a few equilibrium stages of separation are required or when the resistance to mass transfer in the continuous phase is unimportant (e.g., water dispersed when E is very large) does a spray column show promise as a commercial extraction device. These conditions are seldom encountered in a regenerable solvent extraction process. For this reason we will be satisfied if the literature only provides a method of correcting our miniplant spray column data for axial mixing. In the uncommon case where a spray column can be commercially feasible, a conservative estimate of its performance can be made by assuming $Pe_c = 0$ for the large-scale spray column.

Brutvan (1958) measured the continuous-phase axial dispersivity, ε_c, as glass beads dropped through an ascending, continuous water phase by using a step function of tracer. He used four diameters of glass beads from 0.12 to 0.24 inch and three column diameters from 1 to 2 inches and found that ε_c decreased with increasing V_c, increased with increasing V_d, decreased as particle size increased and increased with increasing column diameter, D. Hazlebeck and Geankoplis (1963) also used a step-wise change in concentration of a water soluble tracer to measure ε_c while methyl isobutyl ketone droplets rose through a descending, continuous water phase. They found that ε_c increased linearly with increasing V_c and was independent of V_d; they used only one droplet size and one column diameter of 1.41 inch. Henton and Cavers (1970) measured the turbulent mixing contribution to ε_c in a system where methyl isobutyl ketone droplets rose through a descending water phase by making a steady injection of water soluble tracer and measuring its concentration upstream (with respect to the continuous phase) from the injection point. They made extensive measurements in a 1.5-inch diameter column and a limited number in a 3.0-inch column. They found that ε_c was independent of V_c (intermediate compared to previous studies), decreased with increasing V_c (opposite to the result of Brutvan), increased with increasing droplet size (opposite to Brutvan), and increased with increasing D (in agreement with Brutvan). It is clear from this brief discussion that the present understanding of axial dispersion in spray columns is far from complete.

Despite the lack of agreement among experimental results, Henton, et al. (1973) have attempted to develop several theoretical approaches based principally on their own extensive data (Henton and Cavers, 1970). They suggested an analogy between the flow of a single-phase fluid through a packed bed with a stationary frame of reference and the two-phase flow in a spray column with the frame of reference moving with the droplets. Their treatment leads to the following relationship between a local Peclet number, Pe_c^* (based on droplet diameter, d_p, and slip velocity, V_s), and the dispersed-phase hold-up, ϕ:

$$Pe_c^* = \frac{V_s\ d_p}{\varepsilon_c} = 2.36\ \phi^{1/3} \qquad \text{(B6)}$$

The numerical constant was calculated by assuming that the droplets on the average are located in a lattice arrangement, but it is actually the result of fitting their experimental data from their 1.5 inch column since several lattice arrangements were assumed and the one best fitting the data was accepted.

Equation (B6) does successfully predict an increase of ε_c with increasing droplet diameter and with decreasing V_c as found by Henton and Cavers (1970), but it does not predict an increase in backmixing when the column diameter is increased since the hold-up is not a function of column diameter when a single system is studied at the same superficial velocities of the phases. However, both Brutvan (1958) and Henton and Cavers

(1970) determined experimentally that ε_c increased with increasing column diameter. On the basis of a multiple linear regression analysis of logarithms of several dimensionless variables, Henton, et al., (1973), using their data for 1.5 and 3.0 inch columns, have estimated that Pe_c* increased linearly with (column diameter)$^{-2.82}$. However, from visual observation of the differences in flow patterns, they believe the increase in ε_c in going from the small column to the larger column is primarily the result of large-scale mixing being present only in the larger column.

In the present study we need an estimate of ε_c in a 1.0 inch diameter column operating with superficial velocities and droplet sizes similar to those studied by Henton and Cavers (1970). We have chosen to use equation (B6) to make that estimate and have thus assumed that no large-scale mixing was present in either our 1.0 inch column or in the 1.5 inch column used to develop the correlation. Had we used the factor (column diameter)$^{-2.82}$ to correct the prediction of equation (12), the values of ε_c used to interpret our data would have been about 1/3 as large.

Treybal (1963) recommends that for analysis of mass transfer rates in a spray column, there are three distinct operations: (1) drop formation and release, (2) drop rise (or fall) through the continuous phase, and (3) drop coalescence at the main interface. In a recent review Heertijes and deNie (1971) further divide the stages of mass transfer operations. The general approach is to estimate the mass transfer during drop formation by one of several theoretical relationships and to assume that the product of the overall dispersed-phase mass transfer coefficient, the drop surface area, and the contact time is the same during drop coalescence as during drop formation (Treybal, 1973). Once these estimates have been used to correct for the "end effects," then the mass transfer during drop movement through the partially backmixed continuous phase can be calculated using the dispersion model.

Treybal (1973) shows that the various theories for estimating the dispersed-phase mass transfer coefficient during drop formation, k_{df}, are of the form

$$k_{df} = G_{13}\rho_d\left(\frac{D_d}{\pi\theta_f}\right)^{1/2} \qquad \text{(B7)}$$

where ρ_d = density of dispersed phase,
θ_f = total time for drop formation (contact time),
D_d = solute diffusivity in dispersed phase.

When this mass transfer coefficient is used to calculate the total mass of solute transferred during the time of drop formation, based on the interfacial area of the fully formed drop, A_p, and on the dispersed-phase concentration of the feed solvent, then the constant, G_{13}, calculated from various theories ranges from 0.857 to 3.43, and most of the available data are correlated with G_{13} in the range from 1.3 to 1.8 (Treybal, 1973). On the assumptions that the mechanism for mass transfer in the continuous phase is the same as for the drop phase and that the two mass transfer resistances are additive, the following equation predicts the product of overall dispersed-phase mass transfer coefficient, drop surface area and contact time when G_{13} is chosen as the average of experimental values:

$$K_{df}A_p\theta_f = \frac{1.55\ A_p\ (D_d\theta_f/\pi)^{\frac{1}{2}}}{[1 + m\ (D_d/D_c)^{\frac{1}{2}}]} \qquad \text{(B8)}$$

where ρ_c = density of continuous phase,

D_c = solute diffusivity in continuous phase,

$$m = \begin{matrix} K_d \text{ when solvent is dispersed} \\ 1/K_d \text{ when water is dispersed} \end{matrix}$$

Equation (B8) was used to correct the data from the miniplant for both end effects.

To predict the continuous-phase mass transfer coefficient, k_c, during drop rise (or fall), Treybal (1973) recommends the equation of Ruby and Elgin (1955) which was developed in an actual spray column with a swarm of drops. When the ratio of continuous-phase viscosity, μ_c, to dispersed-phase viscosity, μ_d, is less than 1 (true for operation with water as the dispersed phase and a volatile solvent as the continuous phase), the equation of Hughmark (1967) for single drops agrees well with the equation of Ruby and Elgin (1955). When $\mu_c/\mu_d>1$ (true for volatile solvent dispersed), the single drop equation predicts a value of k_c up to three times larger (Hughmark, 1967) than the preferred value from the Ruby and Elgin equation (1955).

Treybal (1973) recommends an equation based on Hadamard-like internal drop circulation for the calculation of k_d for circulating drops.He also suggests that this expression be corrected for the presence of a continuous-phase resistance by using a result which Elzinga and Banchero (1959) developed for heat transfer. However, several apparent errors were introduced when Treybal (1973) converted their heat transfer result to this mass transfer situation.

In the table presented by Treybal (1973) a dimensionless parameter, $F = k_c d_p/D_c$, was suggested to determine the magnitude of the correction to simple additivity of resistances. However, the correct parameter to use when applying this correction should have been $F = k_c d_p/K_d D_d$ for the two-phase mass transfer situation. The correct factor, F, is proportional to the factor, $R = k_c/K_d k_d$, used by King (1964; 1965) when the usual approximation for long exposure times is made to the equation for k_d (Treybal, 1963). Also, King (1965) showed that the correction to additivity due to an interaction of the two individual-phase mass transfer coefficients results in an increase in the overall mass transfer coefficient. As suggested by Treybal, the Elzinga and Banchero (1959) correction to k_d should actually have been equal to the overall mass transfer coefficient based on the dispersed phase. The treatment used in this project assumes that simple additivity is a sufficiently accurate approximation. This approach is equivalent to using the equation of Kronig and Brink (1950).

For drops larger than a critical size, oscillations in shape occur as the drops fall through a continuous phase. This critical size can be predicted by the terminal velocity correlation of Klee and Treybal (1956). Oscillations not only result in a lower drop terminal velocity, but they also increase the mass transfer coefficient. Treybal (1973) recommends a calculation procedure for k_d in an oscillating drop which is based on the surface stretch theory of Angelo, et al. (1966; 1968). When coupled with the assumption of additivity of mass transfer resistances and the assumption that the same surface stretch mechanism determines the magnitude of k_c, this equation leads to an estimate of K_{oc} for oscillating drops.

Rotating disc contactors. A typical RDC (see Figure 10 in main text) consists of (1) a series of thin discs attached to a central rotating shaft, (2) a series of thin stator plates attached to the vessel walls and located vertically at points midway between the discs, (3) a variable speed drive, and (4) inlet and outlet lines (shown for solvent dispersed with a unique solvent inlet line). The design procedure for an RDC which was described by Treybal (1963) should more precisely be called a scale-up procedure since the equations contain "constants" which have been observed to vary over considerable ranges but which are generally found to remain constant when changes involve only the scale of the device. Since 1963, Misek has published numerous contributions to the understanding of an RDC. Although the description to follow is based on the treatment by Treybal, the more recent results of Misek are also introduced where applicable.

In considering the hydrodynamics of an RDC, it must be realized that an additional variable is introduced in comparison to the spray column extractor. With an RDC the rotational speed of the discs has a fundamental influence on the performance, just as the distributor had on the performance of the spray column. Photographic studies of the drops formed at a spray column distributor plate (Scheele and Meister, 1968) have shown that the majority of interfacial area results from drops which have a very narrow range of diameters. Therefore, it is reasonable to model the spray column in terms of a monodisperse droplet size distribution. Photographic studies of the droplet size distribution in an RDC (Olney, 1964; Misek, 1963a) have shown that a much wider range of droplet diameters exist. Nevertheless, the following discussion illustrates a moderately successful approach to modeling the RDC in terms of an average drop diameter.

Daily and Nece (1960) showed that the torque required to drive an enclosed rotating disc is nearly a unique function of disc Reynolds number;

they observed a slight influence of the ratio of disc diameter to height of the enclosure. Earlier Reman and van der Vusse (1955) developed an equivalent correlation for predicting the power input per compartment, P, for an RDC contactor. Their results were given in the form of a graph of the power number, Po, vs. the disc Reynolds number, Re, defined as follows:

$$Po = \frac{P\ g_c}{\rho_c\ N^3 d_i^{\,5}} \qquad \text{(B9)}$$

$$Re = \frac{d_i^{\,2}\ N\rho_c}{\mu c} \qquad \text{(B10)}$$

where N = rotational speed of the discs
d_i = diameter of the discs.

This correlation can be used to estimate the size of drive required (the power requirement is usually small for waste water treatment), but Equation (B9) can also be used for scale-up when a power per unit liquid mass, $\overline{P/M}$, is defined as follows:

$$\overline{P/M} = \frac{4P_o N^3\ d_i^{\,5}}{\pi g_c\ H_c\ D^2} \qquad \text{(B11)}$$

where H_c = distance between stators
D = column diameter.

One basis for scale-up is to hold $\overline{P/M}$ constant as the dimensions are increased.

Several authors (Olney, 1964; Misek, 1963a) have studied the droplet size distribution in the stirred region of an RDC with the conclusions that, as predicted by the theory of Hinze (1955), there is a maximum droplet size and that the droplet size distribution follows the equation of Mugele and Evans (1951). Strand, et al. (1962) assumed that an average droplet size, d_p, could be used for the calculation of mass transfer rates as well as for flooding and hold-up calculations, and that this average droplet diameter was a constant fraction of the maximum drop diameter predicted by the Hinze equation. This leads to the following equation for d_p:

$$d_p = G_{18} \left(\frac{\sigma}{\rho_c}\right)^{0.6} (\overline{P/M})^{-0.4} \qquad \text{(B12)}$$

where σ = interfacial tension.

Misek (1963a) has presented a more detailed analysis in which he considered that there are two regions, one laminar and the other turbulent, and that the average drop diameter is a different function of N for these two regions. Olney (1964) discussed the limitations of the assumption that a single average drop diameter can be used for estimating both mass transfer and hydrodynamics.

Strand, et al. (1962) have developed a series of relationships which allow the constant G_{18} to be evaluated from hold-up measurements.

They assumed that the characteristic velocity, V_k, defined by equation (B1) is equal to the terminal drop velocity, V_t, multiplied by a constriction ratio, C_R, which is the minimum of (1) the area between the disc and the column, (2) the area within the stator hole, and (3) the area of the frustum of a cone from the stator to the adjoining disc, where each area is divided by the cross-sectional area of the column to form a ratio. This statement can be expressed as follows:

$$V_k = V_t \, C_R \tag{B13}$$

$$C_R = \min \left\{ \begin{array}{l} 1 - (d_i/D)^2 \\ \\ (d_s/D)^2 \\ \\ \left[\dfrac{d_s + d_i}{D}\right]\left[\left(\dfrac{d_s - d_i}{D}\right)^2 + \left(\dfrac{H_c}{D}\right)^2\right]^{1/2} \end{array} \right\} \tag{B14}$$

where d_s = diameter of hole in stator.

V_t can be calculated from C_R and V_k by using equation (B1) and experimental hold-up data; then the relationship between V_t and d_p (Klee and Treybal, 1956) discussed for spray column extractors is used to determine d_p. Finally G_{18} is evaluated from equation (B12). This procedure assumes that for a given system at a given rotational speed, the hold-up is defined by the following with a constant value of V_k:

$$V_s = V_k (1 - \phi) \quad (B15)$$

Misek (1963b) has had considerable success using an alternative equation defining a different characteristic velocity, V_n, as follows:

$$V_s = V_n (1 - \phi) \exp (\phi [W - 4.1]) \quad (B16)$$

where W was defined as a "coalescence coefficient." Misek has correlated V_n (1963a) and W (1964), but later Misek and Rozkos (1966) found in analyzing an industrial RDC used for waste water dephenolization that letting W = 0 gave good results. The constant 4.1 in equation (B16) results from a correlation of the settling of non-aggregating particles (Steinour, 1944).

To summarize the procedure of Strand, et al. (1962) for correlating the hold-up and drop diameter in an RDC, a method is available in which one adjustable parameter, G_{18}, is evaluated from experimental hold-up measurements. Using this value, a graph of Po vs. Re (equations (B9) and (B10), and Reman and van der Vusse, 1955), and equations (B1), (B11), (B12), B13), and (B14), the hold-up and drop diameter at other operating conditions can be established. Olney (1964) has shown that the drop diameter so estimated corresponds to the Sauter mean of the droplet size distribution (i.e., the volume-surface mean diameter). The correlation was shown to work well when no solute transfer was taking place, but a number of unusual observations during mass transfer studies could not be predicted by this method (Strand, et al., 1962). Similar difficulties are described with respect to the present study in Section VIII.

Despite the limitations of any method which models an RDC in terms of a monodisperse droplet size distribution, the above correlation suggests a rational basis for scale-up. Equation ((B12) suggests that if $\overline{P/M}$ is held constant during scale-up, then the average droplet size, d_p, (and hopefully the droplet size distribution) will remain the same. Equations (B13) and (B14) suggest that if the ratios of d_s/D, d_i/D, and H_c/D are held constant, then C_R and V_k (since V_t is fixed by d_p) will remain constant. Finally if V_d and V_c are held constant, then V_s and ϕ will remain constant during scale-up. As discussed later, the importance of axial mixing does not remain constant during this method of scale-up, and its effect must be accounted for separately.

Flooding in an RDC is a much different phenomenon than flooding in a spray column extractor or any other device which produces a narrow range of droplet sizes. Flooding in an RDC actually starts with the entrainment of the smallest droplets along with the continuous phase. As the value of V_c increases, a larger and larger fraction of the dispersed phase is entrained until finally the maximum stable droplet size is entrained and the column is fully flooded.

Nevertheless, several methods of estimating "the flooding velocity" based on an average drop diameter have been reported.

The flooding of an RDC can be estimated from the results of any correlation of V_k using equations (B2), (B3), and (B4). Once G_{18} is evaluated from one experimental measurement as described above, then V_k can be determined. Logsdail, et al. (1957) have given another correlation for V_k that is useful for estimating the flooding point. The relationship based on V_n in equation (B16) has also been analyzed by assuming $\partial V_d/\partial \phi = 0$ at the flooding point (Misek, 1963b).

In an RDC axial mixing takes place in both the dispersed and continuous phases. Much of the work reported on axial mixing in RDC extractors as well as all of the discussion to follow has been developed in terms of the dispersion model. The mechanism for axial mixing in the dispersed phase is quite complex as it involves drop coalescence and redispersion, the distribution of drop velocities due to their size distribution, and radial variation in drop velocity due to vessel geometry and rotating disc speed. Several approaches to correlating the available data are discussed, but these only provide an estimate of ε_d. Axial mixing in the continuous phase is much better understood, and ε_c can be predicted with reasonable accuracy.

A number of studies have dealt with the measurement of ε_c in the absence of a dispersed phase. Westerterp and Landsman (1962) determined

ε_c with water as the continuous phase by using a step injection of salt tracer, and found ε_c could be correlated as the sum of two terms as follows:

$$\varepsilon_c = G_1 N + G_2 V_c \qquad \text{(B17)}$$

where G_1 and G_2 are constants.

Subsequent experiments (Westerterp and Meyberg, 1962) using a steady injection of salt tracer and measuring its concentration upstream showed that the first term in equation (B17) is due to turbulent mixing (which is the only contribution measured in the steady tracer injection) and the second term is due to channeling (i.e., non-uniform axial velocities). Strand, et al. (1962) also determined the separate effects on the total axial dispersion coefficient and correlated their data as follows:

$$\frac{\varepsilon_c}{V_c H_c} = 0.5 + 0.09\left(\frac{d_i\ N}{V_c}\right)\left(\frac{d_i}{D}\right)^2\left(\left[\frac{d_s}{D}\right]^2 - \left[\frac{d_i}{D}\right]^2\right) \qquad \text{(B18)}$$

where H_c = height of one compartment.

This result shows the effect of column dimensions and is of the same form as equation (B17), but it implies that if $d_s = d_i$, the turbulent mixing term tends to zero which is unlikely. This objection was later corrected, resulting in the recommendation of Reman (1966) that the following expression be used:

$$\frac{\varepsilon_c}{V_c H_c} = 0.5 + 0.012 \left(\frac{d_i N}{V_c}\right)\left(\frac{d_s}{D}\right)^2 \qquad \text{(B19)}$$

Other studies (Miyauchi, et al. 1966; Misek, 1965) have led to similar correlations.

It should be pointed out that when using the dispersion model we assume that all the various mechanisms for mixing in the continuous phase (and in the dispersed phase) can be estimated by a single term of a form like that for molecular diffusion (see Appendix C). One of the phenomena this formulation can predict is the experimentally observed jump in concentration at the continuous-phase inlet. However, if we considered both turbulent mixing and channeling in a more accurate mathematical formulation, only turbulent mixing would result in such a concentration jump. Obviously there is an approximation involved in treating both mechanisms as the sum of two contributions to this single term.

Strand, et al (1962) also studied axial mixing in the continuous phase when the dispersed phase was in counter-current flow and found that equation (B18) could be modified to account for the dispersed phase by replacing V_c with $V_c/(1-\phi)$. Making this same modification to equation (B19) leads to the equation used in the present work to estimate ε_c, as follows:

$$\frac{\varepsilon_c(1 - \phi)}{V_c H_c} = 0.5 + 0.012\,(1 - \phi)\left(\frac{d_i\ N}{V_c}\right)\left(\frac{d_s}{D}\right)^2 \qquad (B20)$$

Strand, et al. (1962) tentatively proposed an equation similar to equation (B18) for estimating ε_d as follows:

$$\frac{\varepsilon_d\ \phi}{V_d H_c} = 0.5 + 0.09\phi\left(\frac{d_i\ N}{V_d}\right)\left(\frac{d_i}{D}\right)^2\left(\left[\frac{d_s}{D}\right]^2 - \left[\frac{d_i}{D}\right]^2\right) \qquad (B21)$$

They suggested that this expression would be best at high rotational speeds where axial mixing of the continuous phase is dominated by the turbulent mixing effect and where the low inertia of the small droplets of dispersed phase should cause them to follow the continous phase fluctuations. Stemerding, et al. (1963) found that ε_d did not obey the form of equations (B17) through (B21), but that ε_d was much larger than ε_c such that the ratio $\varepsilon_d/\varepsilon_c$ varied from about 100 to 1. At flooding conditions, the droplet velocity is low so $\varepsilon_d/\varepsilon_c$ is approximately 1, whereas at normal operation at about 80% of flooding, $\varepsilon_d/\varepsilon_c$ is about 10.

For the present study we have used equation (B21) to estimate the dispersed phase axial mixing. While we realize that this is very approximate, there does not seem to be a better solution available. As pointed out by Olney (1964), any attempt to develop a correlation of dispersed-phase axial mixing while assuming a monodisperse droplet size distribution has little hope for success. It should be noted that the error associated with using equation (B21) will be most severe for solutes having a low extraction factor and thus a major mass transfer resistance in the dispersed, solvent phase.

The prediction of mass transfer rates in an RDC, like that for the spray column, is very approximate and requires experimental data to judge between various models. Strand, et al. (1962) suggested that the model for stagnant, noncirculating drops and the model for fully circulating drops should provide limits for the expected mass transfer coefficients. They express these limits as follows:

a. Stagnant drops: $k_c = 0.001\ V_s$ (B22)

$$k_d = \frac{2\pi^2 D_d}{3d_p} \qquad \text{(B23)}$$

b. Circulating drops:

$$k_c = \left(\frac{4\ D_c\ V_s}{\pi d_p}\right)^{1/2} \qquad \text{(B24)}$$

$$k_d = \frac{2\pi^2 D_d}{3d_p} + \frac{0.00375\ V_s}{1 + \mu_d/\mu_c} \qquad \text{(B25)}$$

Equation (B22) is empirical and was apparently first introduced by Strand, et al. (1962). Equation (B23) and the first term in equation (B25) are well established for long exposure times, and the second term in equation (B25) is due to circulation as predicted by Handlos and Baron (1957). Equation (B24) is from penetration theory, and to be precise should include a second term to account for diffusion (Sherwood number equals 2). However, under normal operation the magnitude of the second term is usually less than the expected inaccuracy of the first term, so neglecting it is not unreasonable.

Misek and Rozkos (1966) also considered a third model for the continuous-phase mass transfer coefficient after the theory of Calderbank and Moo-Young (1961). Their expression for k_c includes the power per unit liquid mass, $\overline{P/M}$, defined by equation (B11), and was expressed as follows:

$$k_c = 0.13\ (\overline{P/M})^{1/4}\ D_c^{2/3}\ (\rho_c/\mu_c)^{5/12} \qquad \text{(B26)}$$

This correlation allows for turbulent mass transfer and probably should be added to the terms for diffusion and penetration. However, in their original development Calderbank and Moo-Young evaluated the coefficient while using this as the only term, so it may be best to use it in the form of equation (B26). In the study by Misek and Rozkos (1966) it was concluded that equation (B26) best fit their experimental data for the extraction of phenol from waste water. The expression for k_d used with k_c in equation (B26) could be equation (B25) or the expression for circulating drops discussed in conjunction with the spray column.

To determine the overall mass transfer coefficient in the RDC, the individual-phase mass transfer coefficients were combined according to the assumptions of additivity of resistances. The use of this assumption involves the approximation associated with the interaction of individual resistances as was discussed with respect to the spray column. The correction to additivity due to this effect was shown by King (1965) to result in an increase in K_{oc} of not more than about 20 percent above K_{oc} from simple additivity. However, with the RDC another effect is present due to the distribution of drop sizes. Since the individual-phase mass transfer coefficients depend on drop size in such a way that R ($= k_c/K_d k_d$) is not uniform over the interface, a second correction to additivity is needed. King (1964) has shown for several mass transfer models that this second correction results in a decrease in K_{oc} which can be quite large. Therefore, neglecting this second correction (which can not be quantified easily) could result in a design estimate of K_{oc} from simple additivity which is not conservative.

APPENDIX C

DEVELOPMENT OF THE DISPERSION MODEL

Most of the information in the literature on axial mixing in spray columns and in RDC extractors has been analyzed in terms of the dispersion model. Many of the studies have been discussed in Appendix B; Vermeulen, et al. (1966) have reviewed the literature. In this appendix the basic equations of the dispersion model are developed in terms of quantities found useful in the treatment of waste waters by solvent extraction.

The nomenclature used in this appendix differs slightly from that of the remainder of this report in that the subscript x refers to the aqueous phase and the subscript y to the solvent phase. The equations are developed for flows on a solute-free basis (i.e., F_x = lb. solute-free water/hr) and for concentrations measured in weight ratios (i.e., X = lb. solute/lb. solute-free water). The use of weight ratios is entirely equivalent to using weight fractions for the dilute solutions encountered in most cases described in this dissertation. However, in several cases (notably the extraction of phenol with n-butyl acetate) the concentration of solute in the solvent phase can become large enough to introduce a significant error. The use of weight ratios eliminates the problem of a changing solvent-phase flow rate as long as the two phases are immiscible. With the case of phenol being extracted by n-butyl acetate, K_d measured in weight ratios shows less change with concentration than does K_d measured in weight fractions. The effect of using weight ratios on the validity of the assumption of a constant value of N_{ox} is unknown.

Dispersion Model for Constant K_d.

Consider a section of column as shown in Figure C1. A is the column cross-sectional area, H the total column height, and ϕ the solvent hold-up. The terms for a material balance for the aqueous phase over a differential slice can be expressed as follows:

a. Solute entering at h = h by convection and dispersion

$$F_x X - \rho_x (1 - \phi) A \varepsilon_x \frac{dX}{dh}$$

b. Solute leaving at h = h + dh by convection and dispersion

$$(1 + dh \frac{d}{dh}) (F_x X - \rho_x [1 - \phi] A \varepsilon_x \frac{dX}{dh})$$

c. Solute leaving x-phase by mass transfer

$$K_{ox} a (X - X^*) A dh$$

A material balance for the aqueous phase leads to the following:

$$-F_x \frac{dX}{dh} + \rho_x (1 - \phi) A \varepsilon_x \frac{d^2X}{dh^2} = K_{ox} aA (X - X^*) \quad (C1)$$

A similar treatment for the solvent phase leads to the following:

$$-F_y \frac{dX}{dh} - \rho_y \phi A \varepsilon_y \frac{d^2Y}{dh^2} = K_{ox} a A (X - X^*) \quad (C2)$$

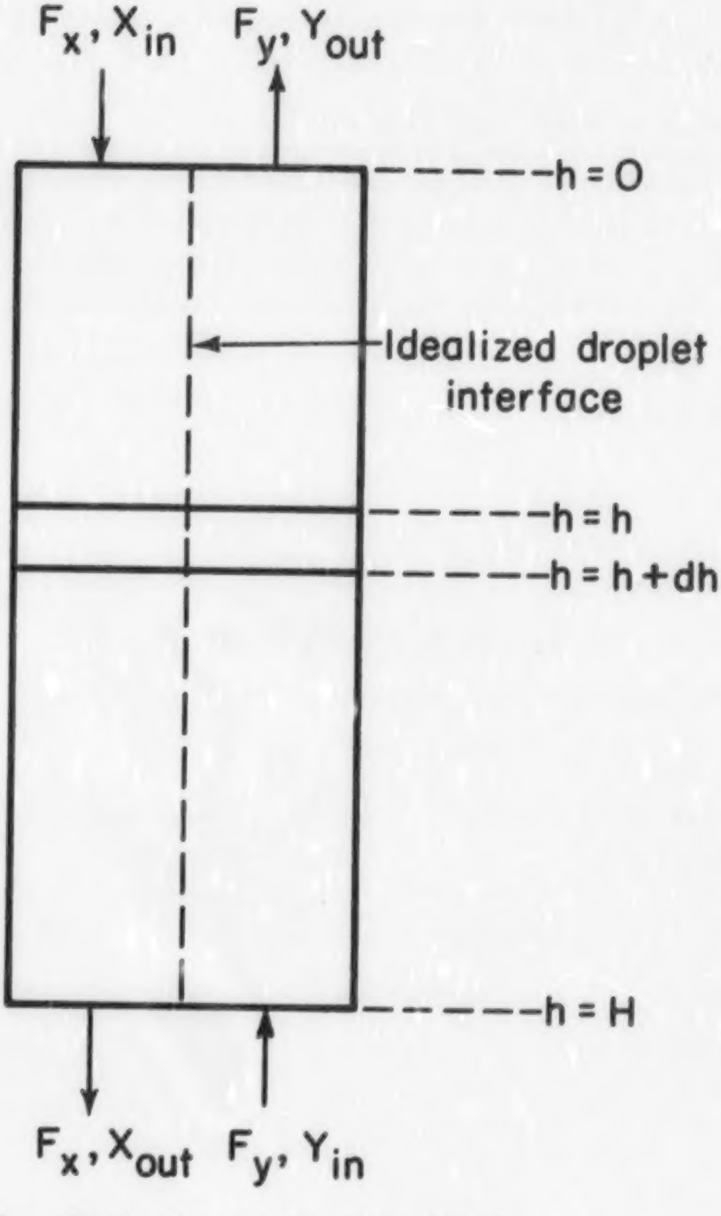

Figure C1. Basis for Dispersion Model

Assuming that the equilibrium may be described by $Y = K_d X^*$ and defining a dimensionless height, $Z = h/H$, lead to the following:

$$-\frac{dX}{dZ} + \frac{1}{Pe_x}\frac{d^2X}{dZ^2} = N_{ox}(X - X^*) \qquad \text{(C3)}$$

$$-E\left(\frac{dX^*}{dZ} + \frac{1}{Pe_y}\frac{d^2X^*}{dZ^2}\right) = N_{ox}(X - X^*) \qquad \text{(C4)}$$

where

$$E = K_d F_y / F_x$$

$$N_{ox} = K_{ox}\ a\ A\ H/F_x$$

$$Pe_x = \frac{F_x H}{\rho_x (1 - \phi)\ A\ \varepsilon_x}$$

$$Pe_y = \frac{F_y\ H}{\rho_y \phi\ A\ \varepsilon_y}$$

Equations (C3) and (C4) are second order, ordinary differential equations in two dependent variables (X and X*) and can be solved once two boundary conditions are specified for each phase.

The usual boundary conditions express the approximation that there is no axial mixing in the inlet or outlet lines. This approximation is expressed as follows:

a. At h = 0 or Z = 0:

$$F_xX - \rho_x(1 - \phi)A\ \varepsilon_x \frac{dX}{dh} = F_xX_{in}$$

or (C5)

$$X_{in} = X - \frac{1}{Pe_x}\frac{dX}{dZ}$$

$$F_yY_{out} + \rho_y\phi A\ \varepsilon_y \frac{dY}{dh} = F_yY_{out}$$

or (C6)

$$\frac{dX^*}{dZ} = 0$$

b. At h = H or Z = 1:

$$F_xX_{out} - \rho_x(1 - \phi)A\ \varepsilon_x \frac{dX}{dh} = F_xX_{out}$$

or (C7)

$$\frac{dX}{dZ} = 0$$

$$F_yY + \rho_y\ \phi\ A\ \varepsilon_y \frac{dY}{dh} = F_yY_{in}$$

or (C8)

$$X^*_{in} = X^* + \frac{1}{Pe_y}\frac{dX^*}{dZ}$$

All the necessary conditions have thus been met for a mathematical solution to be developed.

It is convenient to define a dimensionless, X-phase concentration as follows:

$$\eta = \frac{X - X^*_{in}}{X_{in} - X^*_{in}} \qquad \text{(C9)}$$

The solution to the equations will thus be of the following form:

$$\eta(Z) = f(Z, E, N_{ox}, Pe_x, Pe_y) \qquad \text{(C10)}$$

When Z = 1, X takes on its value in the purified water outlet stream giving the following equation:

$$\eta(1) = f(E, N_{ox}, Pe_x, Pe_y) \qquad \text{(C11)}$$

When Z = 0, X takes on its value at the point within the column where the water is discharged from the inlet line.

Hartland and Mecklenburgh (1966) have shown that the equations (C3) through (C9) may be solved analytically in terms of the roots (q_1, q_2, q_3) of the following equation:

$$q_i^3 + (Pe_y - Pe_x)\ q_i^2 - \left(Pe_x Pe_y + Pe_x N_{ox} + \frac{Pe_y N_{ox}}{E}\right) q_i$$

$$+ Pe_x\ Pe_y\ N_{ox}\ \left(\frac{1}{E} - 1\right) = 0 \qquad \text{(C12)}$$

These authors have set down the analytical solutions for the general case and for a number of cases where simplified equations are possible including the following three cases most important in this report:

1. Pe_x and Pe_y finite; $E = 1$
2. Pe_x finite; $Pe_y = \infty$; $E \neq 1$
3. Pe_x finite; $Pe_y = \infty$; $E = 1$

The listing of a Fortran program developed to carry out these calculations is reproduced at the conclusion of this section.

It should be pointed out that in this development we assume that E, N_{ox}, Pe_x, and Pe_y are constant throughout the column, that there is radial homogeneity at all levels, and that the idealized boundary conditions are satisfied. A treatment where E is not constant is discussed in the following section. Wilburn (1964) has proposed other boundary conditions to account for stagnant liquid in both end sections of the extraction column.

SUBROUTINE EETA

```
      SUBROUTINE EETA(PEX.PEY.E.NOX.ZETA.K.Z.U.V)
C* EETA DETERMINES ZETA WHEN PEX. PEY. E. AND NOX ARE GIVEN.  WHEN K=1.
C*** NO CONCENTRATION PROFILE IS CALCULATED.  WHEN K=2. THE PROFILE IS
C*** CALCULATED AT Z(1) = ZETA(0.0). Z(2) = ZETA(0.1). Z(3) = ZETA(0.2).
C*** Z(4) = ZETA(0.3). Z(5) = ZETA(0.5). Z(6) = ZETA(0.7).
C*** Z(7) = ZETA(0.8). Z(8) = ZETA(0.9). AND Z(9) = ZETA(1.0)
C*** WHEN K=3. ZETA.U(I). AND V(I) ARE CALCULATED FOR I=1.101.
C*** WHEN PEY .LT. 0.0 . CALCULATE FOR INFINITE PEY.
C*** WHEN E .LT. 0.0 . CALCULATE FOR INFINITE E.
C***
      DIMENSION Z(9).U(101).V(101)
      REAL NOX.K1.K2.K3
      IF(PEY.LT.0.0) GO TO 20
      IF(E,EQ.1.0) GO TO 10
C***
C************************** SECTION 1 STARTS HERE **************************
C*** CALCULATE ZETA FOR GENERAL CASE.  FIRST SOLVE CUBIC.
      P = PEY - PEX
      IF(E,LT.0.0) GO TO 1
      Q = -(PEX*PEY + PEX*NOX + PEY*NOX/E)
      R = PEX*PEY*NOX*(1.0/E - 1.0)
      GO TO 2
    1 Q = -(PEX*PEY + PEX*NOX)
      R = -PEX*PEY*NOX
    2 A = (3.0*Q - P*P)/3.0
      B = (2.0*P*P*P - 9.0*P*Q + 27.0*R)/27.0
      C = -(B/2.0)/SQRT(-A*A*A/27.0)
      PHI = ACOS(C)/3.0
      D = 2.0*SQRT(-A/3.0)
      Q1 = D*COS(PHI) - P/3.0
      ADD = 2.0*3.14159/3.0
      Q2 = D*COS(PHI + ADD) - P/3.0
      Q3 = D*COS(PHI + 2.0*ADD) - P/3.0
C*** NOW CALCULATE THE SOLUTION.
      H1 = 1.0 - Q1/PEX
      H2 = 1.0 - Q2/PEX
      H3 = 1.0 - Q3/PEX
      G1 = H1/(1.0 + Q1/PEY)
      G2 = H2/(1.0 + Q2/PEY)
      G3 = H3/(1.0 + Q3/PEY)
      EQ1 = EXP(Q1)
      EQ2 = EXP(Q2)
      EQ3 = EXP(Q3)
      K1 = (G3*EQ2 - G2*EQ3)/Q1
      K2 = (G1*EQ3 - G3*EQ1)/Q2
      K3 = (G2*EQ1 - G1*EQ2)/Q3
      IF(E,LT.0.0) GO TO 3
      DENOM = K1*H1*(1.0 - EQ1/E) + K2*H2*(1.0 - EQ2/E) +
     1 K3*H3*(1.0 - EQ3/E)
      GO TO 4
    3 DENOM = K1*H1 + K2*H2 + K3*H3
    4 IF(K,EQ.1) GO TO 6
      IF(K,EQ.3) GO TO 51
      Z(1) = 1.0 - (K1*(H1 - 1.0) + K2*(H2 - 1.0) + K3*(H3 - 1.0))
     1  /DENOM
      J = 1
      DO 5 I=1,9
      IF(I.EQ.4 .OR. I.EQ.6) GO TO 5
      J = J + 1
      X = FLOAT(I)/10.0
      Z(J) = 1.0 - (K1*(H1 - EXP(Q1*X)) + K2*(H2 - EXP(Q2*X))
     1  + K3*(H3 - EXP(Q3*X)))/DENOM
    5 CONTINUE
    6 ZETA = Z(9) = 1.0 - (K1*(H1 - EQ1) + K2*(H2 - EQ2) + K3*(H3 - EQ3)
     1  )/DENOM
      RETURN
   51 DO 59 I=1,101
      X = FLOAT(I - 1)/100.0
      EQ1X = EXP(Q1*X)
      EQ2X = EXP(Q2*X)
      EQ3X = EXP(Q3*X)
      U(I) = 1.0 - (K1*(H1 - EQ1X) + K2*(H2 - EQ2X) + K3*(H3 - EQ3X))
     1  /DENOM
      V(I) = (K1*(G1*EQ1X - H1*EQ1) + K2*(G2*EQ2X - H2*EQ2) + K3*(G3
     1  *EQ3X - H3*EQ3))/DENOM
   59 CONTINUE
      ZETA = U(101)
      RETURN
C***
C**************************** SECTION 2 STARTS HERE *************************
C*** CALCULATE ZETA FOR E = 1.0 WITH BACKMIXING IN BOTH PHASES.
C*** FIRST SOLVE THE QUADRATIC.
   10 B = PEY - PEX
      C = -(PEX + PEY)*NOX - PEX*PEY
      D = SQRT(B*B - 4.0*C)
      Q2 = (-B + D)/2.0
      Q3 = (-B - D)/2.0
C*** NOW CALCULATE THE SOLUTION.
      H2 = 1.0 - Q2/PEX
      H3 = 1.0 - Q3/PEX
      G2 = H2/(1.0 + Q2/PEY)
      G3 = H3/(1.0 + Q3/PEY)
      EQ2 = EXP(Q2)
      EQ3 = EXP(Q3)
      DENOM = H2*(EQ3 - G3)*(1.0 - EQ2)/Q2 + H3*(G2 - EQ2)*(1.0 - EQ3)
     1  /Q3 - (G3*EQ2 - G2*EQ3)*(1.0 + 1.0/PEX + 1.0/PEY + 1.0/NOX)
      IF(K.EQ.1) GO TO 15
      IF(K.EQ.3) GO TO 16
      Z(1) = 1.0 - ((EQ3 - G3)*(H2 - 1.0)/Q2 + (G2 - EQ2)*(H3 - 1.0)/Q3
     1 - (G3*EQ2 - G2*EQ3)/PEX)/DENOM
      J = 1
      DO 13 I=1,9
      IF(I.EQ.4 .OR. I.EQ.6) GO TO 13
      J = J + 1
      X = FLOAT(I)/10.0
      Z(J) = 1.0 - ((EQ3 - G3)*(H2 - EXP(Q2*X))/Q2 + (G2 - EQ2)*(H3 -
     1  EXP(Q3*X))/Q3 - (G3*EQ2 - G2*EQ3)*(X + 1.0/PEX))/DENOM
   13 CONTINUE
   15 ZETA = Z(9) = 1.0 - ((EQ3 - G3)*(H2 - EQ2)/Q2 + (G2 - EQ2)*(H3 -
     1  EQ3)/Q3 - (G3*EQ2 - G2*EQ3)*(1.0 + 1.0/PEX))/DENOM
```

```
      RETURN
   16 DO 18 I=1,101
      X = FLOAT(I - 1)/100.0
      EQ2X = EXP(Q2*X)
      EQ3X = EXP(Q3*X)
      U(I) = 1.0 - ((EQ3 - G3)*(H2 - EQ2X)/Q2 + (G2 - EQ2)*(H3 - EQ3X)
     1  /Q3 - (G3*EQ2 - G2*EQ3)*(X + 1.0/PEX))/DENOM
      V(I) = ((EQ3 - G3)*(G2*EQ2X - H2*EQ2)/Q2 + (G2 - EQ2)*(G3*EQ3X
     1  - H3*EQ3)/Q3 - (G3*EQ2 - G2*EQ3)*(1.0 - X + 1.0/PEY))/DENOM
   18 CONTINUE
      ZETA = U(101)
      RETURN
C***
C************************** SECTION 3 STARTS HERE **************************
C*** CALCULATE ZETA FOR E .NE. 1.0 WITH NO BACKMIXING IN DISPERSED PHASE
C*** FIRST SOLVE QUADRATIC.
   20 IF(E.EQ.1.0) GO TO 30
      IF(E.LT.0.0) GO TO 21
      B = -(PEX + NOX/E)
      C = NOX*PEX*(1.0/E - 1.0)
      GO TO 22
   21 B = -PEX
      C = -NOX*PEX
   22 D = SQRT(B*B - 4.0*C)
      Q1 = (-B + D)/2.0
      Q2 = (-B - D)/2.0
C*** NOW CALCULATE THE SOLUTION.
      H1 = 1.0 - Q1/PEX
      H2 = 1.0 - Q2/PEX
      EQ1 = EXP(Q1)
      EQ2 = EXP(Q2)
      IF(E.LT.0.0) GO TO 23
      DENOM = H1*(1.0 - EQ1/E)/Q1/EQ1 - H2*(1.0 - EQ2/E)/Q2/EQ2
      GO TO 24
   23 DENOM = H1/Q1/EQ1 - H2/Q2/EQ2
   24 IF(K.EQ.1) GO TO 26
      IF(K.EQ.3) GO TO 27
      Z(1) = 1.0 - ((H1 - 1.0)/Q1/EQ1 - (H2 - 1.0)/Q2/EQ2)/DENOM
      J = 1
      DO 25 I=1,9
      IF(I.EQ.4 .OR. I.EQ.6) GO TO 25
      J = J + 1
      X = FLOAT(I)/10.0
      Z(J) = 1.0 - ((H1 - EXP(Q1*X))/Q1/EQ1 - (H2 - EXP(Q2*X))/Q2/EQ2)
     1  /DENOM
   25 CONTINUE
   26 ZETA = Z(9) = 1.0 - ((H1 - EQ1)/Q1/EQ1 - (H2 - EQ2)/Q2/EQ2)/DENOM
      RETURN
   27 DO 29 I=1,101
      X = FLOAT(I - 1)/100.0
      U(I) = 1.0 - ((H1 - EXP(Q1*X))/Q1/EQ1 - (H2 - EXP(Q2*X))/Q2/EQ2)
     1  /DENOM
      V(I) = (H1*(EXP(Q1*(X - 1.0)) - 1.0)/Q1 - H2*(EXP(Q2*(X - 1.0))
     1  - 1.0)/Q2)/DENOM
   29 CONTINUE
      ZETA = U(101)
      RETURN
```

```
C***
C************************* SECTION 4 STARTS HERE **************************
C*** CALCULATE SOLUTION FOR E = 1. WITH NO BACKMIXING IN DISPERSED PHASE
   30 PN = PEX + NOX
      EPN = EXP(PN)
      DENOM = 1.0 + 1.0/PEX + 1.0/NOX - (1.0 - EPN)*NOX/PEX/PN/EPN
      IF(K.EQ.1) GO TO 35
      IF(K.EQ.3) GO TO 40
      Z(1) = 1.0 - (1.0/PEX - (NOX/PEX + 1.0)/PN/EPN)/DENOM
      J = 1
      DO 33 I=1,9
      IF(I.EQ.4 .OR. I.EQ.6) GO TO 33
      J = J + 1
      X = FLOAT(I)/10.0
      Z(J) = 1.0 - ((1.0/PEX + X) - (NOX/PEX + EXP(PN*X))/PN/EPN)/DENOM
   33 CONTINUE
   35 ZETA = Z(9) = 1.0 - ((1.0/PEX + 1.0) - (NOX/PEX + EPN)/PN/EPN)
     1  /DENOM
      RETURN
   40 DO 45 I=1,101
      X = FLOAT(I - 1)/100.0
      U(I) = 1.0 - ((1.0/PEX + X) - (NOX/PEX + EXP(PN*X))/PN/EPN)/DENOM
      V(I) = (1.0 - X - NOX*(EXP(PN*(X - 1.0)) - 1.0)/PEX/PN)/DENOM
   45 CONTINUE
      ZETA = U(101)
      RETURN
      END EETA
```

Dispersion Model For Varying K_d

Several authors have considered the design of extraction columns which exhibit axial mixing for systems where K_d is not constant. Rod (1964) described a graphical approach which is generally applicable to any shape of the equilibrium curve. Unfortunately his technique requires a time consuming trial and error graphical solution for cases where axial mixing is appreciable in both phases. McSwain and Durbin (1966) developed a computerized solution to the backflow model for systems where K_d is not constant. When the number of stages becomes very large, their solution provides a suitable description of a continuous extractor. However, these authors made the incorrect assumption that the height of an overall transfer unit (or the overall mass transfer coefficient) was constant throughout the column. Recently Pratt (1975) announced an upcoming paper in which a new approach will be described. The technique developed below is similar to the approach of McSwain and Durbin (1966), but the values of the two individual numbers of transfer units (rather than the overall number of transfer units) were assumed to be constant through the column.

Equations (C3) and (C4) derived for the case of a constant K_d were replaced by the following four equations:

$$\frac{dX}{dZ} - \frac{1}{Pe_x}\frac{d^2X}{dZ^2} = -N_x\,(X - X^i) \qquad \text{(C13)}$$

$$\frac{dY}{dZ} + \frac{1}{Pe_y}\frac{d^2Y}{dZ^2} = -N_y\,(Y^i - Y) \qquad (C14)$$

$$(X - X^i) = \frac{N_yF_y}{N_xF_x}\,(Y^i - Y) \qquad (C15)$$

$$Y^i = K_d{}^i\,X^i \qquad (C16)$$

In these equations the superscript i refers to concentrations at the interface between phases. Since we assumed that the value of $K_d{}^i$ was known once the value of X^i or Y^i was determined, the above system of equations involved two new variables (Y^i and X^i) and two new equations and was determinant once the boundary conditions were specified. Boundary conditions equivalent to those in the previous section were written as follows:

a. At $Z = 0$:

$$X_{in} = X - \frac{1}{Pe_x}\frac{dX}{dZ} \qquad (C17)$$

$$\frac{dY}{dZ} = 0 \qquad (C18)$$

b. At $Z = 1$:

$$\frac{dX}{dZ} = 0 \qquad (C19)$$

$$Y_{in} = Y + \frac{1}{Pe_y}\frac{dY}{dZ} \qquad (C20)$$

To develop a numerical solution to this set of equations, the column was divided into (N-1) cylinders of equal length such that $Z_1 = 0$, $Z_2 = h$, $Z_3 = 2h, \ldots, Z_N = 1$. At all points, from Z_2 to Z_{N-1} equations (C13) and (C14) were written in terms of central finite differences. For example, at any point Z_i for $2 \leq i \leq N-1$, equation C13 became

$$\frac{(X_{i+1} - X_{i-1})}{2h} - \frac{1}{Pe_x} \frac{(X_{i+1} - 2X_i + X_{i-1})}{h^2} = N_x(X_i - X_i^i).$$

When the terms were collected in a way which left X_i^i on the right hand side, this equation became

$$- \frac{1}{2h} + \frac{1}{Pe_x h^2} X_{i-1} + N_x + \frac{2}{Pe_x h^2} X_i + \frac{1}{2h} - \frac{1}{Pe_x h^2} X_{i+1}$$

$$= N_x X_i^i.$$

At the points Z_1 and Z_N the central difference equations were written in terms of two imaginary points Z_0 and Z_{N+1}, and then the boundary equations were used to eliminate these points from the system of equations. This results in the following matrix of equations:

$$\underline{\underline{A}}\ \underline{X} = \underline{g} \tag{C21}$$

$$\underline{\underline{B}}\ \underline{Y} \quad \underline{f} \tag{C22}$$

where the terms in the vectors $\underline{X}$, $\underline{Y}$, $\underline{g}$, and $\underline{f}$ are as follows:

X_i = concentration in X phase at Z_i
Y_i = concentration in Y phase at Z_i

$$g_1 = N_x X_1^{\,i} + (Pe_x + \frac{2}{h})\, X_{in}$$

$$g_i = N_x X_i^{\,i} \qquad i = 2, 3, \ldots, N$$

$$f_i = N_y Y_i^{\,i} \qquad i = 1, 2, \ldots, N-1$$

$$f_N = N_y\, Y_N^{\,i} + (Pe_y + \frac{2}{h})\, Y_{in}$$

$\underline{\underline{A}}$ and $\underline{\underline{B}}$ are tridiagonal matrices defined as follows:

$$\underline{\underline{A}} = \begin{bmatrix} s_1 & t_1 & 0 & 0 & . & . \\ r_2 & s_2 & t_2 & 0 & . & . \\ 0 & r_3 & s_3 & t_3 & . & . \\ . & . & . & . & . & t_{N-1} \\ . & . & . & . & r_N & s_N \end{bmatrix}$$

where

$$r_i = -\left(\frac{1}{2h} + \frac{1}{Pe_x h^2} \right) \qquad i = 2, 3, \ldots, N-1$$

$$r_N = -\frac{2}{Pe_x h^2}$$

$$s_1 = N_x + Pe_x + \frac{2}{Pe_x h^2} + \frac{2}{h}$$

$$s_i = N_x + \frac{2}{Pe_x h^2} \qquad i = 2, 3, \ldots, N$$

$$t_1 = -\frac{2}{Pe_x h^2}$$

$$t_i = \frac{1}{2h} - \frac{1}{Pe_x h^2} \qquad i = 2, 3, \ldots, N-1$$

$$\underline{\underline{B}} = \begin{bmatrix} v_1 & w_1 & 0 & 0 & . & . \\ u_2 & v_2 & w_2 & 0 & . & . \\ 0 & u_3 & v_3 & w_3 & . & . \\ . & . & . & . & . & w_{N-1} \\ . & . & . & . & u_N & v_N \end{bmatrix}$$

where

$$u_i = \frac{1}{2h} - \frac{1}{Pe_y h^2} \qquad i = 2, 3, \ldots, N-1$$

$$u_N = \frac{2}{Pe_y h^2}$$

$$v_i = N_y + \frac{2}{Pe_y h^2} \qquad i = 1, 2, 3, \ldots, N-1$$

$$V_N = N_y + Pe_y + \frac{2}{Pe_y h^2} + \frac{2}{h}$$

$$w_1 = - \frac{2}{Pe_y h^2}$$

$$w_i = - \left(\frac{1}{2h} + \frac{1}{Pe_y h^2}\right) \qquad i = 2, 3, \ldots, N-1$$

Equations (C21) and (C22) involved four unknown vectors $\underline{X}$, $\underline{Y}$, $\underline{X}^i$, and $\underline{Y}^i$. When equations (C15) and (C16) were also written for each value of Z_i, there were four vector equations available in terms of these four unknowns.

All the elements of matrices $\underline{\underline{A}}$ and $\underline{\underline{B}}$ are constant for the case where N_y, N_x, Pe_y and Pe_x are constant. The inverses of these matrices were determined at the beginning of the calculation, which resulted in the following:

$$\underline{X} = \underline{A}^{-1} \underline{g} \qquad \text{(C23)}$$

$$\underline{Y} = \underline{B}^{-1} \underline{f} \qquad \text{(C24)}$$

This completes the development of equations.

This set of equations was used for two types of problem. One problem was encountered when two solutes which interact strongly were present in the feed water at fairly high concentrations. For example, when n-butyl acetate at about 6000 ppm and phenol at about 300 ppm were present in a feed waste water which was treated by isobutylene extraction, the presence of n-butyl acetate in the solvent led to a much higher efficiency of phenol removal than was expected based on the K_d for phenol between water and pure isobutylene. The numerical approach was used in this case by assuming that the presence of phenol had little effect on the n-butyl acetate extraction so that the concentration profile for n-butyl acetate was predicted from the linear model. Equations (C15) and (C16) were then used to determine Y^i_{BA} from which K^i_{phenol} was determined. The solution then proceeded as follows:

a. Set $\underline{X}$ and $\underline{Y}$ at initial values determined from the linear model,

b. Determine $\underline{X}^i$ and $\underline{Y}^i$ from equations (C15) and (C16),

c. Determine $\underline{g}$ and $\underline{f}$ from their definitions,

d. Determine new values of $\underline{X}$ and $\underline{Y}$ from equations (C23) and (C24), and

e. Return to step b., and iterate to convergence. The results of these calculations are discussed in Section VIII.

The second situation where this method of solution was useful was in determining the effect of a variation in K_d for one solute due to a change in its own concentration. For example, when phenol was present at about 3 pounds of phenol per 100 pounds of feed water in a water stream which was treated by n-butyl acetate extraction, the value of K_d changed significantly through the column. The results of using this numerical approach to analyze this case are discussed below.

Several characteristics of this numerical calculation were observed for both types of problem. The accuracy of the numerical result as a function of the grid size (h) was estimated by comparing the converged numerical solution to the analytical solution for the case of the constant K_d. Some results from such calculations are shown in Table C1 for a case where the parameters were similar to those for the extraction of phenol with recycled n-butyl acetate in the miniplant. The concentration profile at the end of the extractor where the solute concentration was lowest (from which % removal was calculated) was accurately predicted with ten column segments. However, the concentration profile at the other end of the extractor (as characterized by Y_{out}) was not very accurately predicted with fewer than fifty column segments. No significant improvement in accuracy was gained by using greater than fifty

Table C1. Results from Sample Numerical Calculation

Parameters:

$N_x = 8.0$ $N_y = 8.0$

$Pe_x = 6.0$ $Pe_y = 25.0$

$F_y/F_x = 0.1$ $K_d = 57.0$

$X_{in} = 0.03$ lb solute/lb feed water

$Y_{in} = 0.02$ lb solute/lb feed solvent

Results:

N - 1	% Removal	Y_{out}
10	95.80	0.3678
20	95.75	0.3233
50	95.74	0.3098
Analytical	95.73	0.3072

column segments, and percent removal was accurately estimated with only ten segments.

In all cases tested, the direct substitution iteration procedure which was described above converged toward the final solution. However, the rate of convergence was very slow and became even slower as the final solution was approached. Several acceleration methods were attempted with little success; usually the calculation then diverged. The most successful acceleration method was to make at least three direct substitution iterations followed by one extrapolation toward the solution using the Wegstein formula (Lapidus, 1962). This procedure usually converged in about one-half the number of iterations required for pure direct substitution. One procedure which was more successful in reducing computation time than any acceleration method was first to solve the problem with ten column segments, then to interpolate to obtain an initial solution for the calculation using twenty or fifty column segments.

For almost all pollutants considered in this dissertation, the value of K_d could be assumed to be constant at the value taken on at infinite dilution. The reasons for this observation are illustrated by considering the overall driving force based on aqueous-phase concentration,

$$\Delta X = X - X^* \qquad (C25)$$

where X is the aqueous-phase concentration at any elevation in the column and X* is the concentration of a hypothetical aqueous phase which would be in equilibrium with the solvent-phase concentration at the same elevation. For the case of a constant K_d

$$X^* = Y/K_d \qquad (C26)$$

at all points in the column. When K_d varies with concentration, the overall driving force given by equation (C25) is still valid as long as equation (C26) is used with K_d evaluated at X^* and Y.

At the solvent inlet end of the extractor (neglecting the concentration jump for the present discussion), the solvent is nearly pure ($Y \approx 0$), so that $K_d = K_d^\infty$. Three factors tend to make Y large at the solvent outlet end of the extractor: (1) efficient extraction, (2) low F_s/F_w, and (3) high concentration of solute in the inlet water. These factors tend to be mutually exclusive; for example, efficient extraction and low F_s/F_w imply a large K_d, which implies a limited water solubility. Even if the feed water is saturated with an easily extracted solute, Y at the solvent outlet will seldom be larger than 0.05 lb solute per lb solvent. At this concentration $K_d = K_d^\infty$ is usually still a good approximation.

One case considered in this report where the above argument did not hold was in the extraction of phenol with n-butyl acetate. Since $K_d^\infty = 57.0$, 95% removal was possible when $F_s/F_w = 0.1$. If the feed water contained 0.03 lb. phenol per lb. water (about one-third of saturation), then $Y = 0.285$ lb. phenol per lb. solvent. The data of Won (1974) are shown in Figure C2 and are compared to the empirical curve

$$K_d = 57.0 - 28.3Y \qquad (C27)$$

which appears to correlate the data up to about 50%

phenol in the n-butyl acetate phase. At Y = 0.285 the value of $K_d = 48.9$, which was a significant decrease from K_d^{∞}.

The numerical method of calculation was used for the case of phenol extraction using n-butyl acetate as solvent. Equation (C27) was used to predict K_d^i in Equation (C16). The calculation predicted 96.59% removal of phenol and Y = 0.2898 lb. phenol per lb. n-butyl acetate for the conditions listed in Table C2. Therefore, $K_d = 48.80$ at the solvent outlet, and $K_d = 52.74$. The results of calculations using the linear model and an average K_d are shown in Table C2. The results showed that using K_d^{∞} gave a good estimation of the removal efficiency, and that using the geometric mean gave almost exactly the correct answer.

A number of calculations like that just described were made for various values of the parameters. In all cases the results showed that the geometric mean value of K_d gave a better approximation than the arithmetic mean. The results also showed that in all cases except when the phenol concentration in the feed water was greater than about 5 weight %, the linear approximation using $K_d = 57.0$ gave a good estimation of overall removal, but a slight improvement was possible by using the geometric mean K_d.

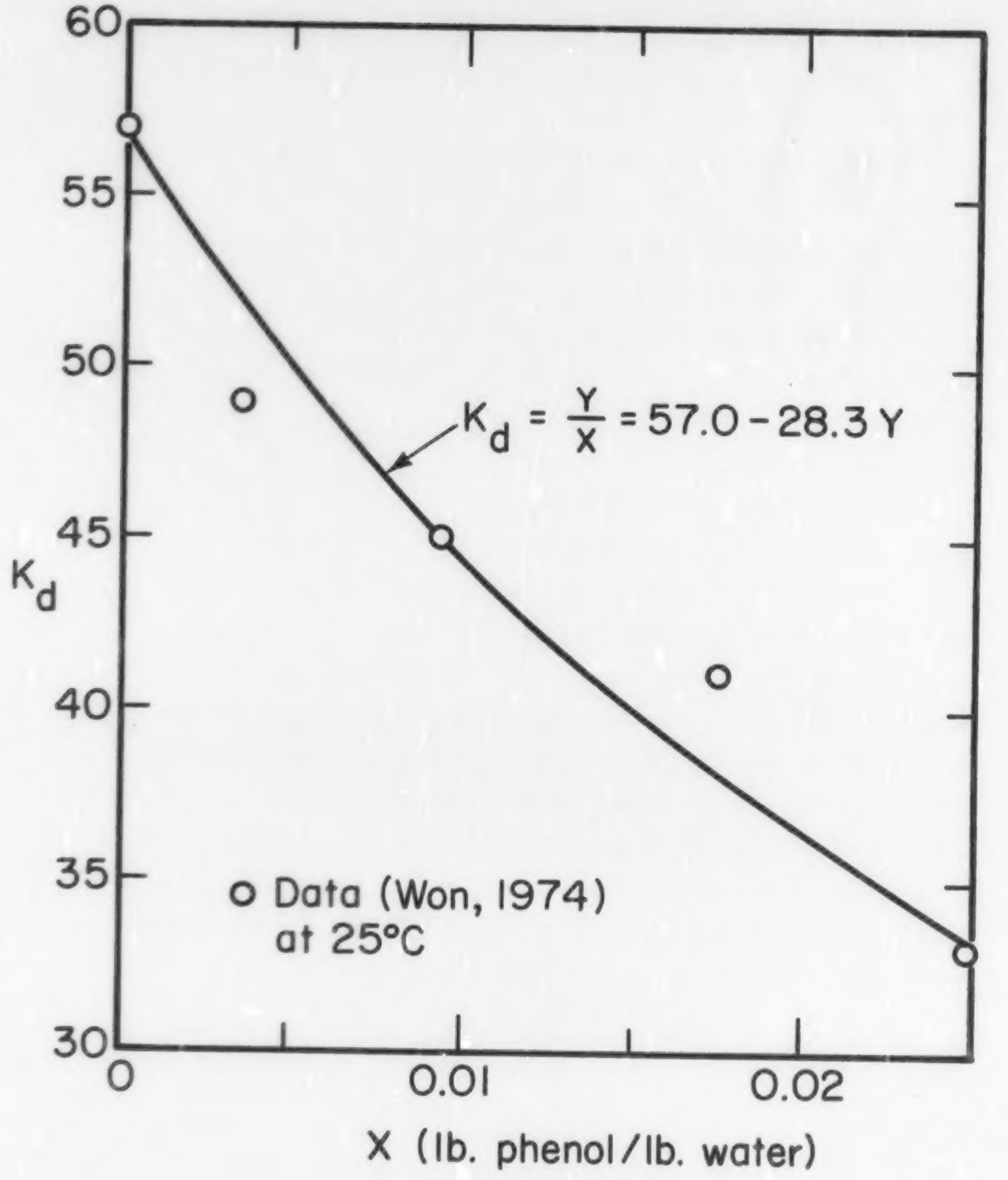

Figure C2. Distribution of Phenol Between Water and n-Butyl Acetate

Table C2. Linear Approximation for K_d Varying with Solute Concentration

Parameters:

$N_x = 8.0$ $N_y = 8.0$

$Pe_x = 6.0$ $Pe_y = 25.0$

$F_y/F_x = 0.1$

$X_{in} = 0.03$ lb. phenol/lb. water

$Y_{in} = 0.00$ lb. phenol/lb. n-butyl acetate

Numerical Calculation:

$K_d = 57.0 - 28.3Y$

% Removal = 96.59

Linear Approximation:

K_d	(K_d basis)	% Removal
57.00	(Inlet solvent)	96.87
52.90	(Arithmetic mean)	96.61
52.74	(Geometric mean)	96.60
48.80	(Outlet solvent)	96.30

APPENDIX D

ALTERNATIVE PROCESSES FOR VOLATILE SOLVENT DISTILLATION

In the volatile solvent extraction process using a C_4 hydrocarbon as solvent, the majority of the total cost is usually associated with the distillation step for solvent regeneration. In this appendix methods of minimizing this distillation cost are discussed and illustrated, using the separation of isobutylene from ethylene dichloride as an example. The conclusions should also apply with slight modification to the volatile solvent extraction of any other pollutant of volatility comparable to that of ethylene dichloride.

The loaded solvent from the extractor will be a relatively dilute solution of pollutant in the volatile solvent at about 80°F. After pumping to the pressure of the distillation column, the feed stream will thus be a subcooled liquid consisting of a wide-boiling mixture. During the separation, all the solvent must be boiled and then condensed. Since this involves a substantial amount of heat supplied and removed, careful consideration must be given to heat economy.

In Section IV we consider a process that uses isobutylene (IB) to remove 95% of the ethylene dichloride (EDC) from a 80°F waste water which contains 0.8% EDC and flows at 100 GPM. The concentration of EDC in the loaded solvent depends on the solvent-to-water flow ratio, F_s/F_w, while the concentrations of EDC in the regenerated solvent (distillate) and in the recovered pollutant (bottom product) do not depend on F_s/F_w but rather are fixed by the required extraction efficiency and by the required product purity (or allowed solvent loss), respectively. For 95% EDC recovery and 1.5% IB in the product EDC, these stream concentrations are listed in the table below along with the total flow of feed as a function of F_s/F_w.

Mole fraction IB in distillate = 0.9968

Mole fraction IB in bottom product = 0.0271

F_s/F_w	Mole fraction IB in feed	Feed Flow Rate (lb mol/hr)
1.50	0.9940	1335
0.70	0.9907	625
0.30	0.9826	270
0.08	0.9454	74.3

For each value of F_s/F_w, there is an optimum distillation column design which results in minimum cost. In this appendix we attempt to locate this optimum by designing and determining alternative costs for several levels of the specified variables and for several process arrangements. The alternative cost is the sum of the annual operating costs (steam, cooling water, and pump power) and the total investment (pumps, heat exchangers, distillation column and tanks) multiplied by 0.259, as is developed in Appendix A. The following assumptions are made in determining the design and cost estimates:

1. Murphree vapor stage efficiency is 0.75.
2. The reboiler provides one equilibrium stage.
3. The distillation column contains bubble cap trays with 18-inch tray spacing and provides a 3-minute liquid hold-up at the bottom.
4. The overall heat transfer coefficient is 200 Btu/hr ft^2 °F in the condenser and reboiler.
5. The condenser cooling water is heated from 80°F to 100°F.
6. The reflux tank provides a 10-minute liquid hold-up.
7. The liquid leaving the extractor has a pressure of 51.4 psia and a temperature of 80°F.

For the distillation column design, vapor-liquid equilibria for the IB-EDC binary system are estimated by the Chao-Seader (1961) method. The large increase in temperature down the column and the fact that the molar heat of vaporization of EDC is almost twice that of IB makes heat effects important and rules out the constant molar overflow assumption. The molar flows tend to decrease down the column, resulting in operating lines on a McCabe-Thiele diagram which are concave upward in the rectifying section and concave downward in the stripping section. Stream enthalpies are estimated by using gas and liquid heat capacities and heats of vaporization for the pure components and by estimating heats of mixing using regular solution theory for the liquid phase and the Redlich-Kwong equation of state for the vapor phase.

First consider the case where $F_s/F_w = 1.5$, which results in a loaded feed that is very dilute in EDC. By assuming that the distillate is condensed at 120°F, the column pressure is determined as 81.1 psia. If the feed is pumped to this pressure and fed to the column as a subcooled liquid, then no reflux is needed and the feed enters the top plate. A stage-to-stage calculation indicates that 5 actual stages are required as shown in Figure D1. Details on the top two plates are illustrated in Figure D2. Operation in this case results in large flows of liquid and vapor throughout the column at near total reflux (L/V varies from 1.0048 below the feed plate to 1.0025 above the reboiler). The reboiler operates at 275°F, so all the heat required to boil the volatile solvent must be supplied at a high temperature. The alternative cost for this case is $129,600 per year with the breakdown shown in Table D1. The steam used to drive the reboiler accounts for 56% of the total alternative cost.

One alternative to the above operation is to vaporize the feed before it is added to the column. If the distillate is again condensed at 120°F, the dew point of the feed is 122°F, so this vaporization can be carried out using exhaust steam. By assuming that reflux is added to the column at 40% above minimum reflux, a stage-by-stage calculation shows 6 plates are required below the feed and 3 plates above.

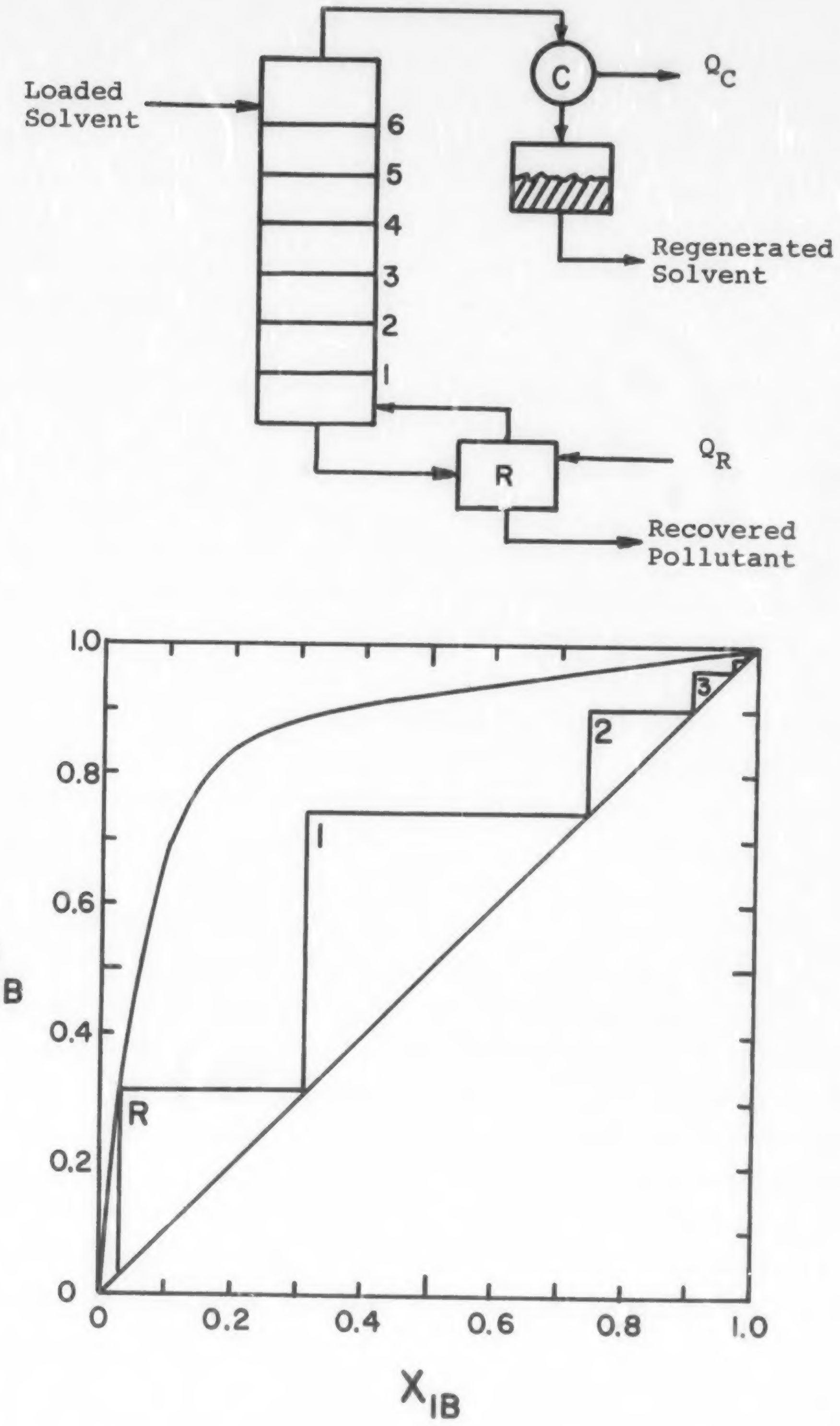

Figure D1. Simplest Alternative

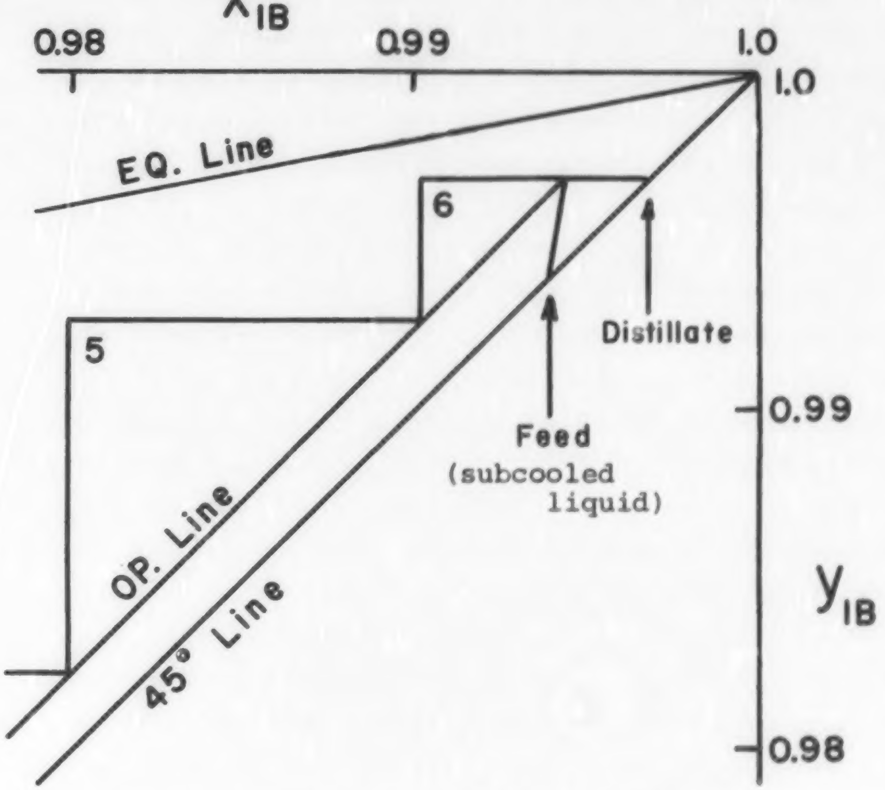

Figure D2. Details of Simplest Alternative

Table D1. Costs for Simplest Alternative

Alternative Investment = $132,000

Equipment Item	% of Total
Condenser	35
Reboiler	29
Distillation Column	26
Solvent Recycle Pump	4
Reflux Tank	6

Alternative Operating Cost = $129,600 /year

Cost Item	% of Total
Capital Cost	26
Cooling Water	17
Steam (100 psig)	56
Power	1

This mode of operation is illustrated in Figure D3 with details of the top few stages shown in Figure D4. Although more total plates are required with a saturated vapor feed than with a subcooled liquid feed, the flows in the stripping section are much lower with the vapor feed (V/F = 0.156 as compared to V/F = 1.17), resulting in a less expensive distillation column. The requirement of a small amount of reflux (R/D = 0.165) results in more total heat required in the feed vaporizer and the reboiler, but the use of cheaper exhaust steam in the feed vaporizer results in a substantial savings. The alternative cost for the case of a saturated vapor feed is $106,900 per year with the breakdown shown in Table D2. The alternative cost is reduced by about 18%.

To fix the design of the distillation column with the saturated vapor feed, it is necessary to assume the condensation temperature and the reflux ratio. Holding the ratio of actual to minimum reflux at 1.4, the effect on the alternative cost due to changing the condensation temperature, and thus the column pressure, was investigated. As the pressure increases, the temperature driving force in the condenser increases while the driving forces in the feed vaporizer and in the reboiler decrease. Also, the cost of the recycle pump and its power increase as temperature and pressure increase. The overall alternative cost decreases rapidly until the distillate temperature reaches 120°F, and then the cost shows a flat minimum between 120 and 140°F. The use of 120°F for cost comparisons seems reasonable.

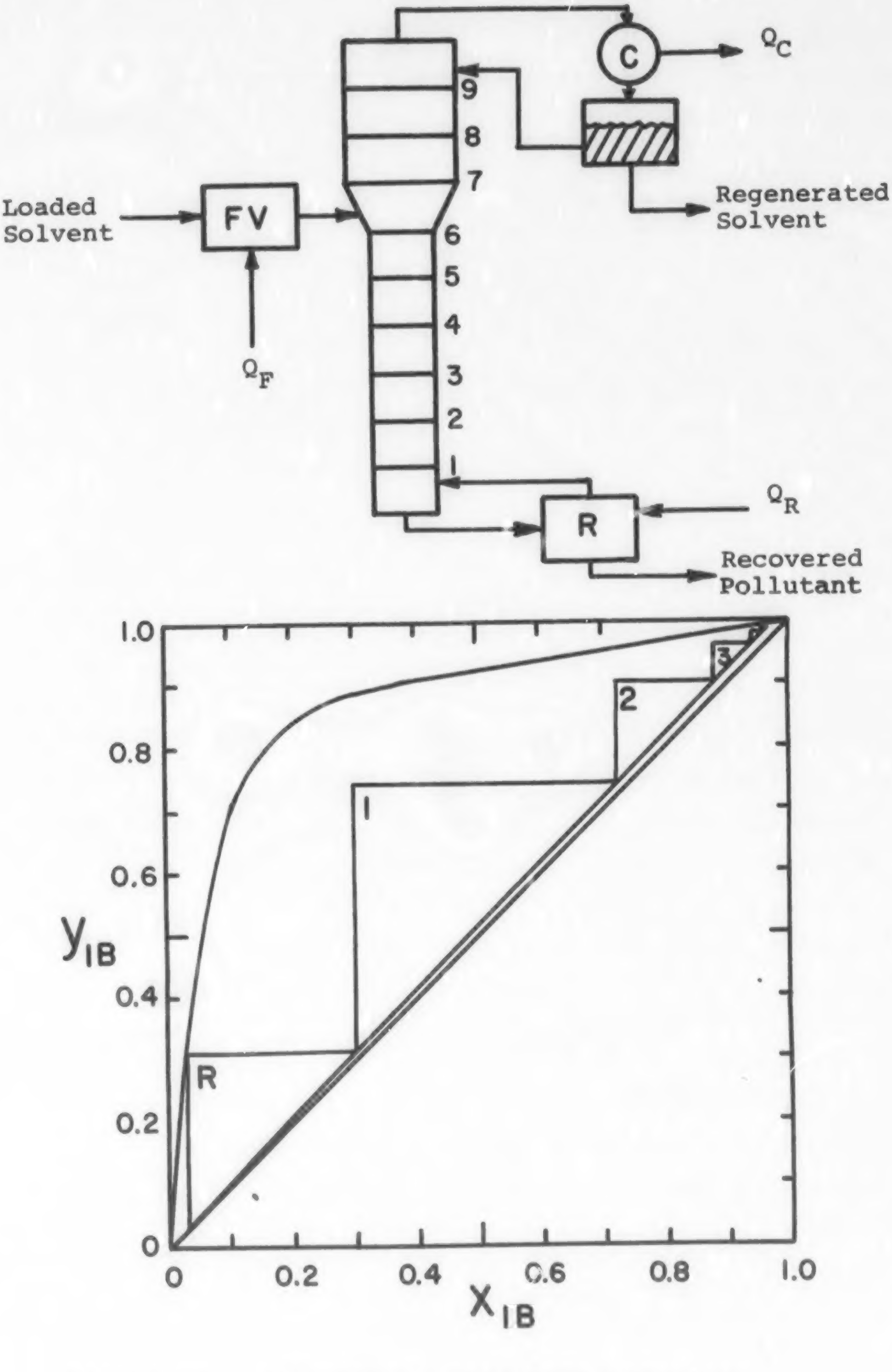

Figure D3. Alternative with Feed Vaporizer

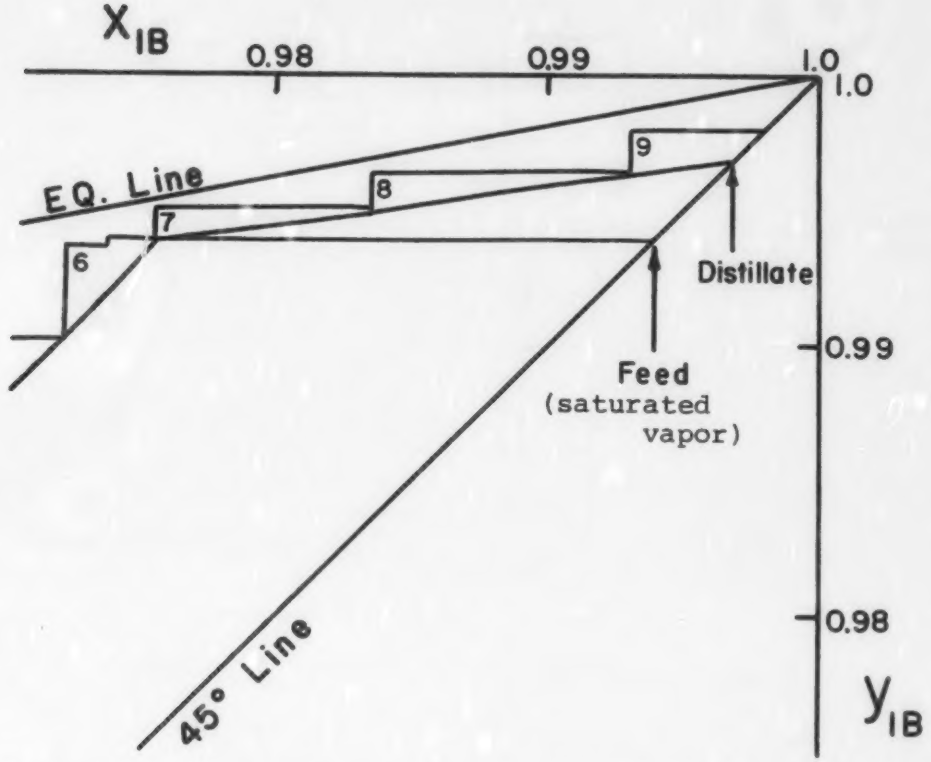

Figure D4. Details of Alternative with Feed Vaporizer

Table D2. Costs for Alternative with Feed Vaporizer

Alternative Investment = $127,900

Equipment Item	% of Total
Condenser	40
Reboiler	8
Feed Vaporizer	20
Distillation Column	19
Pumps	6
Reflux Tank	7

Alternative Operating Cost = $106,900 /year

Cost Item	% of Total
Capital Cost	31
Cooling Water	24
Steam (100 psig)	10
Steam (Exhaust)	34
Power	1

Another alternative arrangement utilizes a subcooled liquid feed (and no reflux), but several stages below the feed point the downflowing liquid is drawn off and partially vaporized. To fix the design in this arrangement, the condensation temperature is set at 120°F, the actual-to-minimum vapor flow in the stripper is set at 1.2, and the temperature of the side stream boiler is varied to locate the optimum. As the side stream boiler is moved up the column and operates at decreasing temperatures, the number of stages and the flows of liquid and vapor in the lower section of the column increase causing an increase in the cost of this portion of the column; however, the number of stages above the side stream boiler decreases, resulting in a nearly constant cost for the entire column. The lower portion of the column is small in all cases and is designed as a packed tower assuming its total height to be the same as a plate tower with 18 inch plate spacing. As the side stream boiler temperature decreases, its temperature driving force and cost decrease, but the portion of the constant amount of total heat which is supplied with higher cost steam in the reboiler increases. An optimum alternative cost of $89,000 per year occurs when the side stream boiler operates at 128°F resulting in 3 stages above and 4 stages below the side stream boiler. This mode of operation is illustrated in Figure D5 with details in Figure D6, and a breakdown in costs is shown in Table D3. The lower portion of the column is designed to operate with $V/F = 0.024$ at 40% of flooding in a 14-inch diameter column packed with 1-inch Raschig rings.

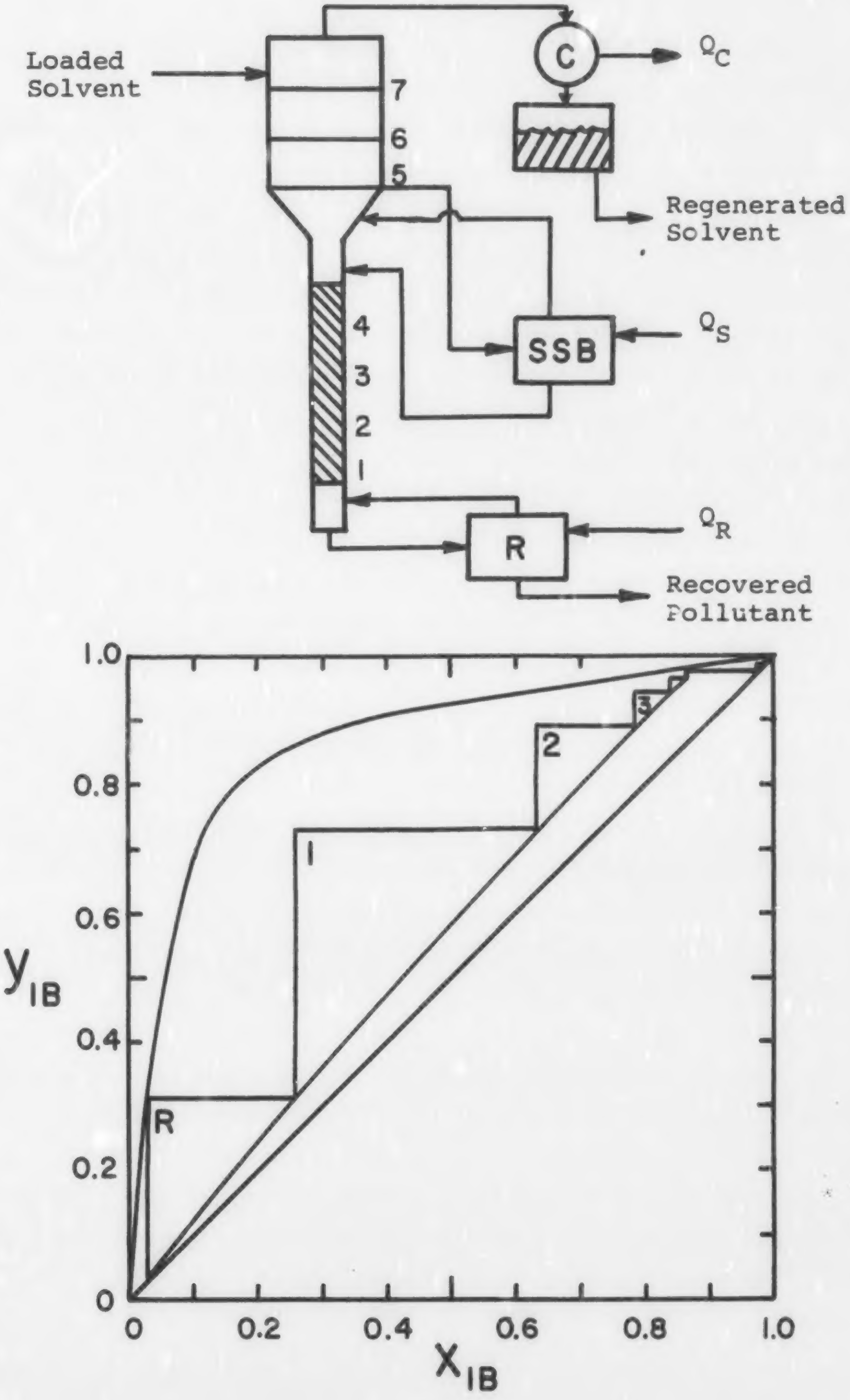

Figure D5. Alternative with Side Stream Boiler

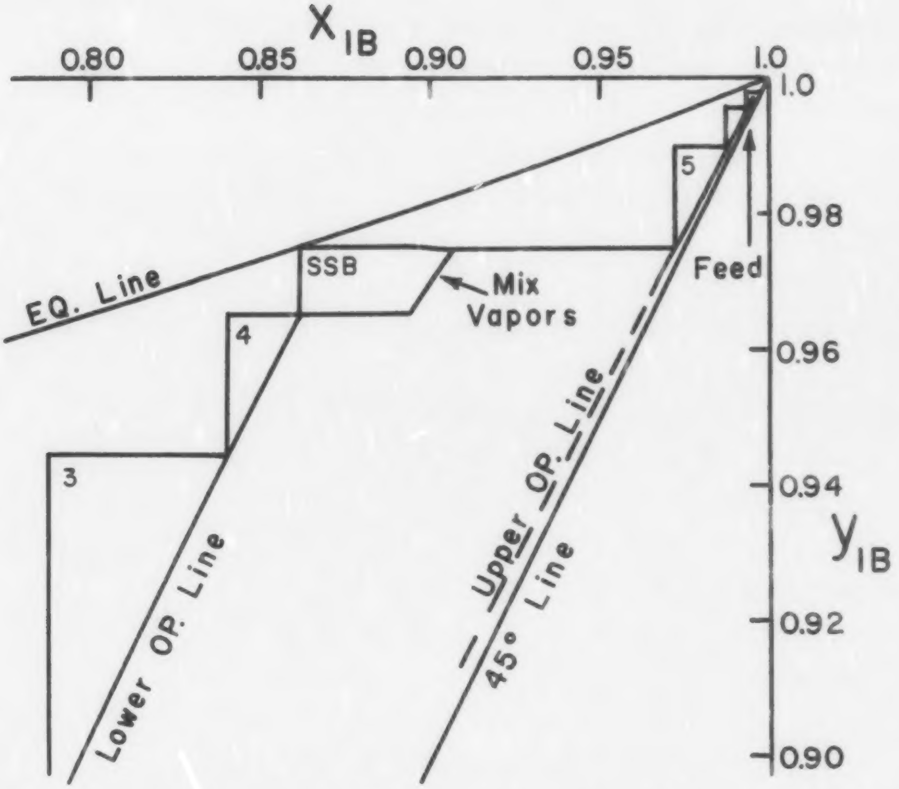

Figure D6. Details of Alternative with Side Stream Boiler

Table D3. Costs for Alternative with Side Stream Boiler

Alternative Investment = $111,500

Equipment Item	% of Total
Condenser	42
Reboiler	1
Side Stream Boiler	28
Distillation Column	17
Solvent Recycle Pump	5
Reflux Tank	7

Alternative Operating Cost = $89,000 /year

Cost Item	% of Total
Capital Cost	32
Cooling Water	25
Steam (100 psig)	2
Steam (Exhaust)	40
Power	1

In comparing the vapor feed and side stream boiler alternatives, the latter results in a 17% lower alternative cost. This lower cost is the result of operating without reflux and thus with smaller quantity of heat supplied and removed, with a smaller condenser and reflux tank, and with no reflux pump. Also, a smaller fraction of the total heat supplied is in the form of high pressure steam with a side stream boiler.

Many of the conclusions discussed for the case where $F_s/F_w = 1.5$ also hold for lower values of F_s/F_w. When $F_s/F_w = 0.08$, reflux is required even with a subcooled liquid feed. The alternative costs for subcooled liquid feed with one reboiler, for saturated vapor feed, and for subcooled liquid feed with a side stream boiler are $14,600/yr., $11,700/yr., and $10,400/yr., respectively. Although all items of equipment are smaller because much less solvent must be regenerated at lower values of F_s/F_w, the cost of the distillation column decreases only moderately with decreasing F_s/F_w and then makes up a larger fraction of the total cost. The optimum location of the side stream boiler is approximately the same for all values of F_s/F_w between 1.5 and 0.08 (i.e., at a point where the temperature is about 128°F). At values of F_s/F_w below about 0.15, the flow of purified water is large enough so that it may replace the need for cooling water in the condenser.

The general procedure recommended for the design of a distillation system for separating any pollutant of similar volatility to ethylene dichloride is to use a subcooled liquid feed and a side stream boiler. Practical operation can be achieved by setting the ratio of actual to minimum reflux at 1.4 (if any reflux is needed), by condensing the C_4 hydrocarbon solvent at 120°F, by setting the ratio of actual to minimum vapor flow below the side stream boiler at 1.2, and by locating the side stream boiler several stages below the feed point. These four parameters can be optimized for any pollutant at a later stage in process development.

APPENDIX E

DISTRIBUTION COEFFICIENTS FOR ORGANIC SOLUTES BETWEEN ISOBUTYLENE OR ISOBUTANE AND WATER*

Introduction

This work presents distribution coefficients for a variety of organic solutes between water and isobutane or isobutylene. Because of the solvent's volatility, it is not possible to use standard apparatus to measure distribution coefficients. A special sampling device was constructed to facilitate sampling of the volatile liquid mixture at pressures ranging from 3 to 10 atmospheres.

Apparatus

The equilibrium cell, shown in Figure E1, is a cylindrical, stainless-steel container about 30 cm long and 12 cm outside diameter. The inside diameter is about 8 cm and the inside depth is 25 cm. Above the top plate is a rotating holding magnet driven by a variable-speed motor. A stirrer rotating inside the equilibrium cell is magnetically coupled to the variable-speed motor. To allow visual observation of the immiscible mixtures under

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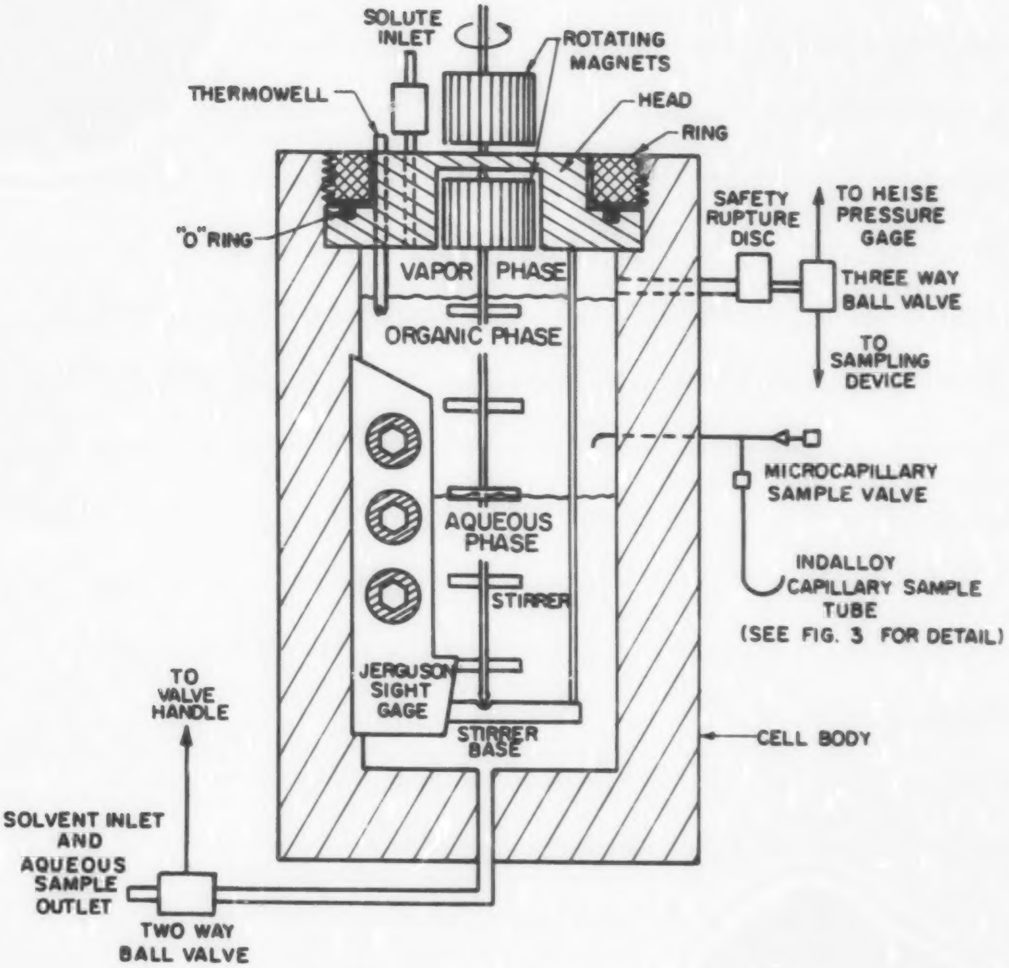
* References and Nomenclature for this Appendix are included at the end of the Appendix.



SCHEMATIC OF EQUILIBRIUM CELL ASSEMBLY

Figure E1

pressure, two Jerguson sight gages are bolted to the two opposite sides of the cylinder. The equilibrium cell is completely immersed in a constant-temperature water bath held at 25 ± 0.05°C. A periscope is positioned outside the front sight gage and a light source is located in the rear. Sampling devices are attached to the side and to the top plate, which also contains a high-pressure, sample-injection port. The pressure is measured by a Heise gage and the temperature in the cell is measured by a liquid-filled glass thermometer with a 0.1°C graduation. Liquefied gas is introduced from an inverted cylinder into the equilibrium cell driven by its own vapor pressure augmented by helium gas at about 1 or 2 atm. All connections are 3.18mm and 6.35mm stainless-steel tubing. Ball valves are from Whitey Research Company. Chemical analysis of both aqueous-phase and organic-phase samples is achieved with a Perkin-Elmer 990 Gas Chromatograph.

Procedure

To start, about 1 liter of distilled water is introduced into the equilibrium cell. Organic solute is introduced with a syringe through a rubber septum located at the top of the cell. Liquefied isobutane (or isobutylene) is then introduced from an inverted gas cylinder.

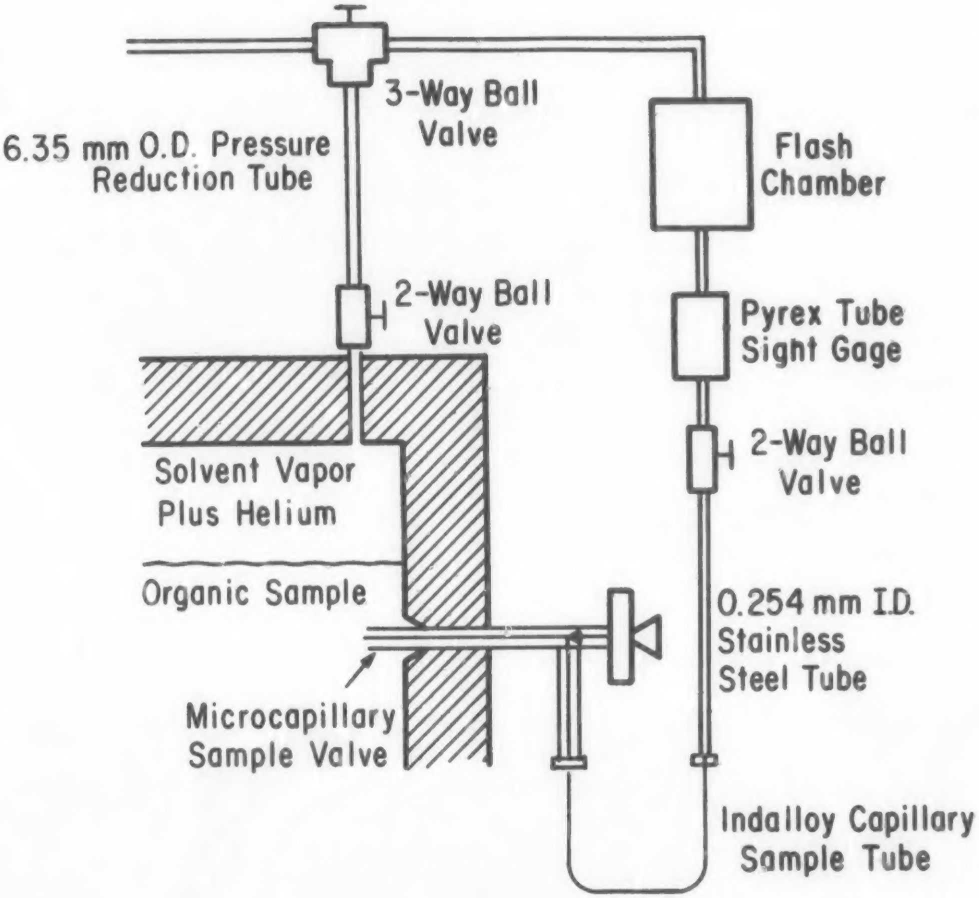
Equilibration between the two phases is obtained by a stirring rod with five propellers, two in each liquid phase and one at the liquid-liquid interface. The two liquid phases are stirred for about ten hours and one hour of settling (no stirring) is allowed before sampling.

Sampling

The aqueous sample is removed at the bottom of the equilibrium cell. After purging twice, a 50-cm^3 sample is removed from the equilibrium cell. From this large sample, six samples, 5 microliters each, are introduced in the chromatograph for chemical analysis. Reproducibility of this analysis is better than 2%.

Because of the high vapor pressure, it is much more difficult to obtain a sample of the organic phase for chemical analysis. Figure E? / shows the special technique devised for sampling of a volatile liquid; this technique is based on the special properties of Indalloy, as suggested by Fleck (1967), based on the work of Nerheim (1964). Initially the flash chamber and the sight gage are filled with solvent vapor and helium gas. After opening the microcapillary sample valve, the pressure in the flash chamber is reduced by opening the 3-way ball valve to the atmosphere. Liquid is allowed to flow into and through the Indalloy capillary sample tube until it fills the Pyrex-tube sight gage.

The Indalloy capillary sample tube is swaged at both ends and removed. This capillary tube, 12 centimeters long, 1.59 mm outer diameter and 0.254 mm internal diameter, is then swaged at intermediate points so as to provide six encapsulated samples, each about one and a half centimeter long, with a volume of approximately 0.5 microliter.


3-Way Ball Valve
6.35 mm O.D. Pressure Reduction Tube
Flash Chamber
2-Way Ball Valve
Pyrex Tube Sight Gage
2-Way Ball Valve
Solvent Vapor Plus Helium
Organic Sample
0.254 mm I.D. Stainless Steel Tube
Microcapillary Sample Valve
Indalloy Capillary Sample Tube

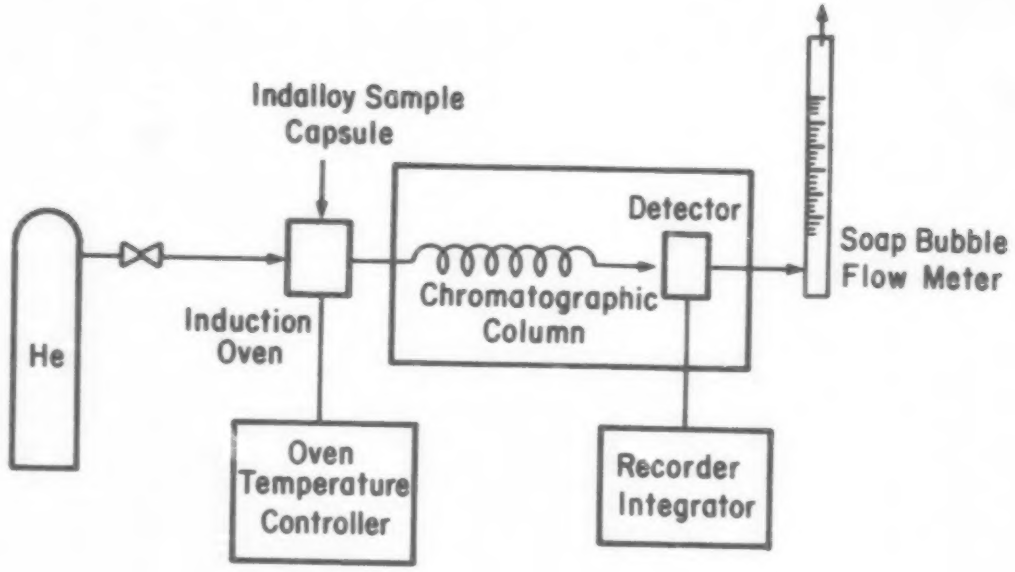
INDALLOY ENCAPSULATION SAMPLING DEVICE

Figure E2

One at a time, each sample is placed into the induction oven as shown in Figures E 3 / and E4 /. The oven [Varian Aerograph Model 695], operating at 250°C, melts the Indalloy (melting point 150°C) and completely vaporizes the sample. Helium gas sweeps the vaporized sample into the chromatograph. Reproducibility is better than 5%. Further details of this analytical procedure are presented elsewhere (Won 1974).

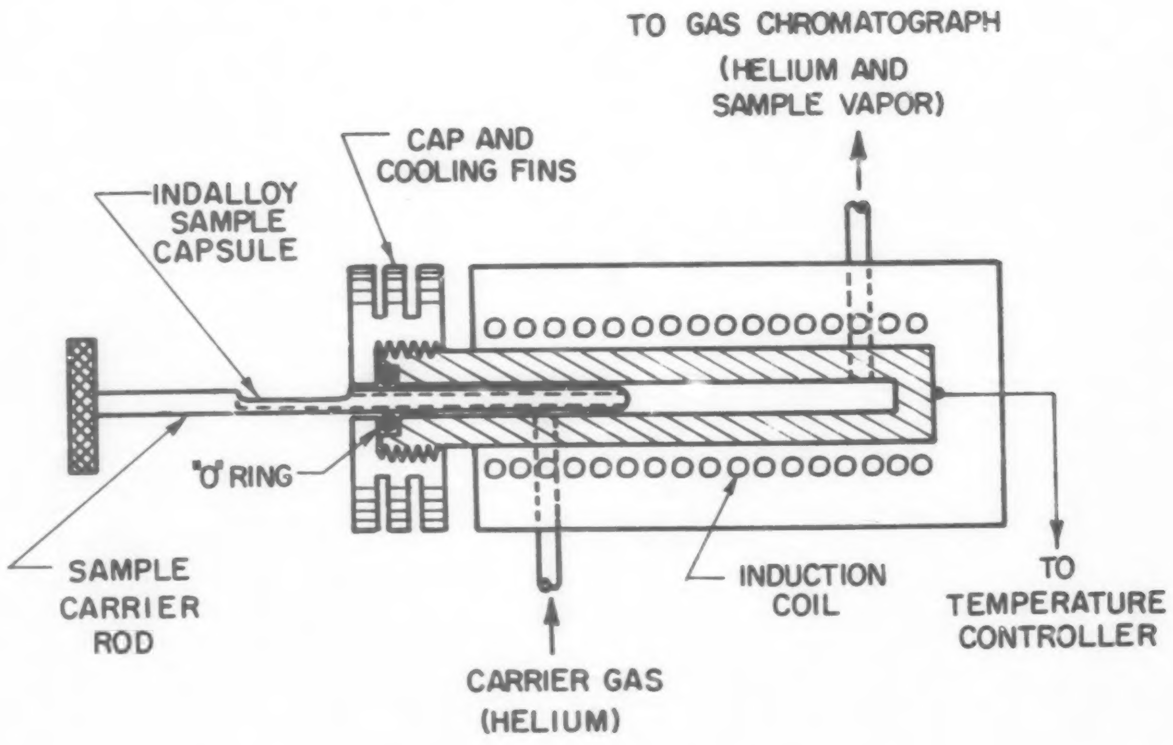
Chemical Analysis

The chromatograph uses two hydrogen-flame-ionization detectors and has linear temperature-programming capability. Two 3. 18mm O. D. stainless-steel tubes, each 1 meter long, are packed with 80-100 mesh Porapak Q (or T). Helium, the carrier gas, flows at 30 cm^3/min at ambient temperature. The detector signals are recorded by a 1. 0mv Brown Electronik recorder equipped with a disc-chart integrator. Temperatures of injector block, detector manifold and induction oven are normally kept at 250°C. Since the volatilities of solvent and solutes are widely different, temperature programming is normally employed, typically from 125°C to about 50°C above the normal boiling point of the heaviest solute. To convert peak area to mass, the response factor (mv sec/mg) of the volatile solvent is obtained as a function of sample size by injecting a known amount of the sample with a calibrated, gas-tight syringe made by Micro-Sampling Corporation. The response factors of the solutes are obtained from chromatograms for mixtures of known composition.



CHEMICAL ANALYSIS INSTRUMENTATION. GAS CHROMATOGRAPH AND INDUCTION OVEN

Figure E3



INDUCTION OVEN FOR MELTING OF INDALLOY SAMPLE CAPSULE

Figure E4

Results

Distribution coefficients were measured for dilute solutions of acetates, ketones, aldehydes and phenolics. These coefficients, in units of $\frac{\text{mole solute/1000 g solvent}}{\text{mole solute/1000 g water}}$ are shown in Tables E1 to E4.

For polar solutes, the distribution coefficients in isobutylene are larger than those in isobutane because of weak complexing between the double bond in isobutylene and the polar group of the solute. For a homologous series, the distribution coefficient increases sharply as the molecular weight of the solute rises.

Correlation of Results: Theory of Dilute Solutions

To interpret and correlate the experimental results, it is convenient to introduce some simplifying assumptions which are applicable to dilute solutions. Let c stand for concentration of the solute, let single prime refer to the aqueous phase and let double prime refer to the organic phase.

Let $\Delta \bar{g}$ stand for the change in partial molar Gibbs energy of the dilute solute when it is transferred at constant temperature and pressure from the aqueous phase to the organic phase such that its concentration is the same in both phases: $c' = c''$. The partial Gibbs energy of transfer is related to the solute concentration and activity coefficients γ by

$$\Delta \bar{g} = RT \ln \frac{c''\gamma''}{c'\gamma'} = RT \ln \frac{\gamma''}{\gamma'} \qquad \text{(E1)}$$

Table E1

Distribution Coefficients and Characteristic Volumes for Acetates. Distribution Between Water and Isobutylene (and Isobutane) at 25°C.

	Distribution Coefficient K†		V^*
	Isobutylene	Isobutane	cm^3/mole
Methyl Acetate	2.56	1.47	80
Ethyl Acetate	10.2	5.86	101
Butyl Acetate	168	107	144
Amyl Acetate	727	(400)	168‡

---

† $K \equiv \frac{\text{mole of solute/1000 g solvent}}{\text{mole of solute/1000 g water}}$

‡ Estimated

( ) Extrapolated

Table E2

Distribution Coefficients and Characteristic Volumes for Ketones. Distribution between Water and Isobutylene (and Isobutane) at 25°C.

	Distribution Coefficient K		V^*
	Isobutylene	Isobutane	$cm^3/mole$
Acetone	0.63	0.33	74
Butanone-2	2.49	1.35	92
Pentanone-3	13.4	(5.5)	112
Methyl Isobutyl Ketone	41.5	24.4	134
Heptanone-2	222	(110)	157[‡]

[‡] Estimated

( ) Interpolated or Extrapolated

Table E3

Distribution Coefficients and Characteristic Volumes for Aldehydes. Distribution between Water and Isobutylene (and Isobutane) at 25°C.

	Distribution Coefficient K		V^*
	Isobutylene	Isobutane	cm^3/mole
Crotonaldehyde	2.48	1.37	88[†]
Butyraldehyde	8.05	4.36	92
Furfuraldehyde	1.44	(0.78)	92
Valeraldehyde	(32.2)	17.2	112[†]
Hexylaldehyde	130	(68.6)	132[†]

[†] Estimated

( ) Interpolated or Extrapolated

Table E4

Distribution Coefficients and Characteristic Volumes for Phenolics. Distribution between Water and Isobutylene (and Isobutane) at 25°C.

	Distribution Coefficient K		V^*
	Isobutylene	Isobutane	cm^3/mole
Phenol	0.7	0.2	98
o-Cresol	4.8	(1.28)	116
m-Cresol	2.7	(0.7)	119
3,5-Xylenol	(7)	2.14	139

( ) Interpolated or Extrapolated

Note that $\Delta\bar{g}$ is not the change in Gibbs energy when phases and " are in equilibrium.

From the definition of Gibbs energy

$$\Delta\bar{g} = \bar{g} - \bar{g}' = \Delta\bar{u} - T\Delta\bar{s} + P\Delta\bar{v} \tag{E2}$$

$$\text{where} \quad \Delta\bar{u} = \bar{u}'' - \bar{u}'$$

$$\text{and} \quad \Delta\bar{s} = \bar{s}'' - \bar{s}'$$

$$\Delta\bar{v} = \bar{v}'' - \bar{v}'$$

In a dilute solution, the partial molar entropy of a solute is determined primarily by its concentration; intermolecular forces between solute and solvent are only of secondary importance. However, the partial molar energy of the solute is strongly dependent on these forces. For the process under consideration here ($c' = c''$), we assume $\Delta\bar{s} = 0$.

At the modest pressures considered here, $P\Delta\bar{v}$ is negligible compared to $\Delta\bar{u}$. To obtain an expression for $\Delta\bar{u}$ we use a concept provided by the perturbed-hard-sphere theory (Reed and Gubbins 1973). We assume

$$\bar{u}' - u^0 = k'q + U' \tag{E3}$$

and

$$\bar{u}'' - u^0 = k''q + U'' \tag{E4}$$

where superscript zero refers to the ideal-gas state at system temperature, q is a (hard-sphere) size parameter for the solute and k' and k'' are (temperature-dependent) constants of proportionality. The characteristic energy U' refers to (attractive) interactions between solute and water and U" refers to similar interactions between solute and organic solvent. Equations (E3) and (E4) follow from the notion that in order to introduce a solute molecule into the liquid solvent, it is first necessary to create a vacancy (hole) of size q. The work required to make the hole in the aqueous phase is k'q and that to make the hole in the organic phase is k"q. Attractive forces between solute and water are responsible for energy U' and those between solute and organic solvent are responsible for energy U".

Substitution gives for the Gibbs energy of transfer

$$\Delta \bar{g} = -kq - \Delta U \tag{E5}$$

where $k = k' - k''$ and $\Delta U = U' - U''$.

The distribution coefficient K is defined by

$$K = \frac{c''_{eq}}{c'_{eq}} = \frac{\gamma'_{eq}}{\gamma''_{eq}} \tag{E6}$$

where subscript eq stands for equilibrium. Since both phases are dilute with respect to solute, we assume that the activity coefficients are constants, independent of concentration; that is, we assume

$$\gamma' \text{ (at } c') = \gamma'_{eq} \text{ (at } c'_{eq}) \quad \text{and} \quad \gamma'' \text{ (at } c'') = \gamma''_{eq} \text{ (at } c''_{eq}) \tag{E7}$$

Substitution of Equations (E5), (E6) and (E7) into Equation (E1) gives the desired result

$$\ell nK = \left(\frac{kq}{RT}\right) + \frac{\Delta U}{RT} \qquad (E8)$$

Among others, McGowan (1954), and Deno and Berkheimer (1960) have used Equation (E8), setting size parameter q equal to the parachor.

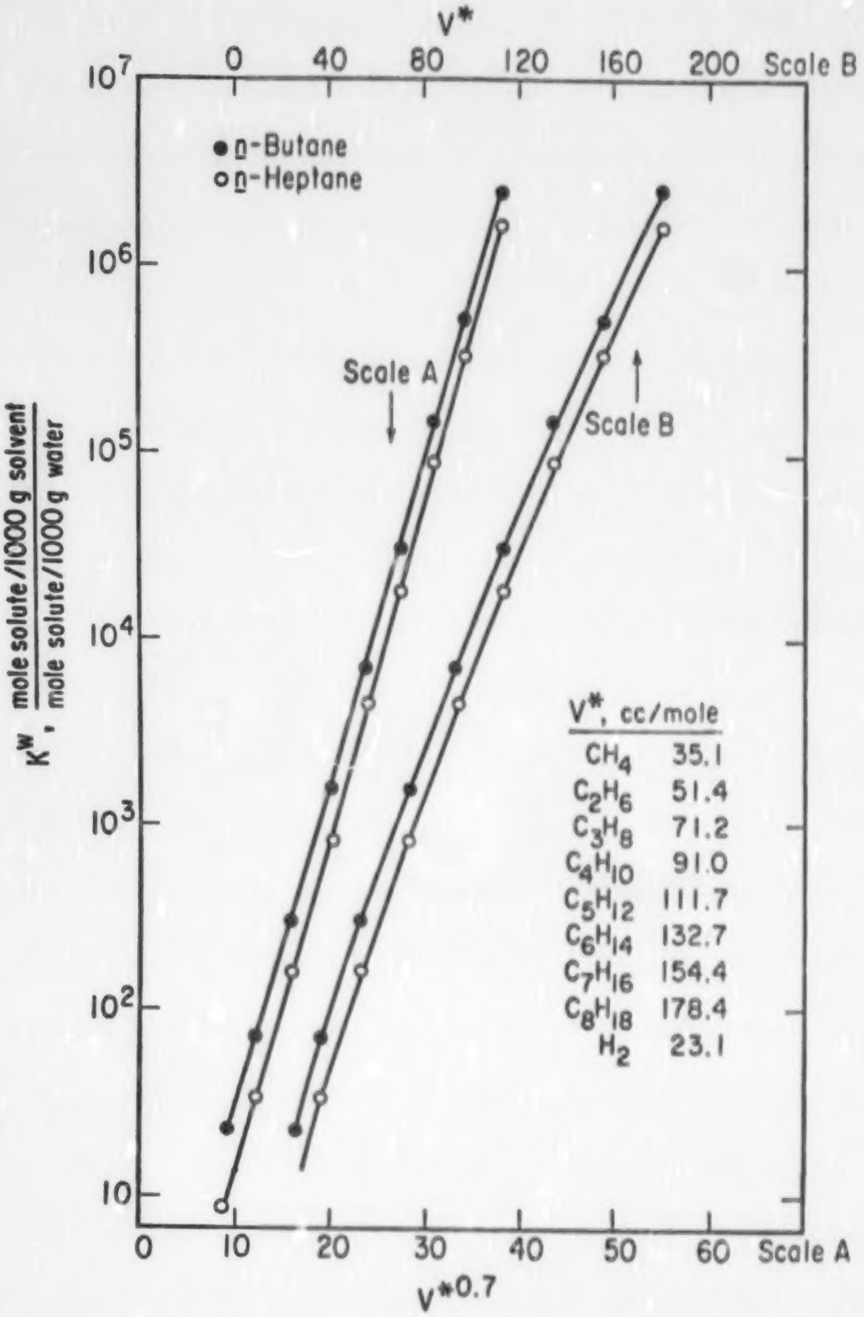
Since the parachor is a poorly understood quantity we prefer to base q on a parameter V^* reflecting the molecular volume. This parameter is calculated from vapor-pressure and density data as outlined subsequently. We have found that the experimental results are better correlated with V^* than with any other commonly-available measure of molecular size.

It can be argued that the energy needed to make a hole for introducing a solute is proportional not to the volume of a solute molecule but to its surface area. Hence we propose to use for q the characteristic volume V^* raised to a constant power m where m is somewhere between 2/3 and unity. To fix m, we investigated the distribution coefficients of paraffins between water and n-butane (or n-heptane) shown in Table E5; these distribution coefficients were calculated from solubility data for hydrocarbons in water (McAuliffe, 1966) and from Henry's constant data in hydrocarbons (Cook et al., 1957; Aroyan et al., 1951; Hayduk et al., 1970, 1973). As indicated by Figure E5 Equation (E8) is obeyed when

Table E5

Distribution Coefficients and Characteristic Volumes for n-Alkanes Between Water and n-Butane (and n-Heptane) at 25°C.

	Distribution Coefficient K		
	n-Butane	n-Heptane	V^*, cm^3/mole
Methane	70.6	33.2	35.1
Ethane	300	159	51.4
Propane	1577	825	71.4
Butane	7040	4000	91.0
Pentane	3.24×10^4	1.67×10^4	111.7
Hexane	1.5×10^5	9.05×10^4	132.7
Heptane	5.33×10^5	3.4×10^5	154.4
Octane	2.53×10^6	1.7×10^6	178.4
Hydrogen	21.2	8.7	23.6



V^*, cc/mole	
CH_4	35.1
C_2H_6	51.4
C_3H_8	71.2
C_4H_{10}	91.0
C_5H_{12}	111.7
C_6H_{14}	132.7
C_7H_{16}	154.4
C_8H_{18}	178.4
H_2	23.1

DISTRIBUTION COEFFICIENTS *vs.* CHARACTERISTIC VOLUMES FOR n-ALKANES BETWEEN WATER AND n-BUTANE (AND n-HEPTANE) AT 25°C

Figure E5

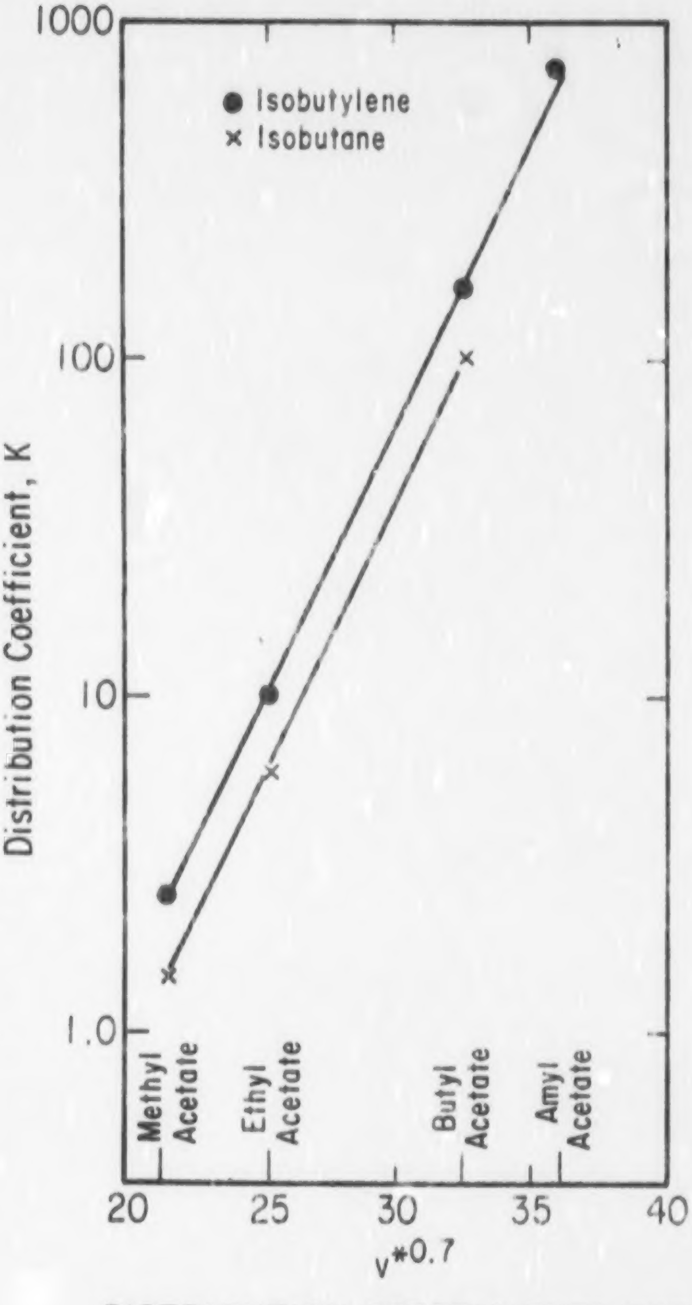
$q = V^{*m}$ with $m = 0.7$. When $m = 0.7$ a plot of log K versus V^{*m} gives a straight line. However, considerable curvature is observed when m is set equal to unity. In all subsequent correlations, we use $m = 0.7$. The constants in Equation (E8) were evaluated by least-squares; they are shown in Table E6.

The experimentally-determined distribution coefficients are plotted on semilogarithmic coordinates as suggested by Equation (E8); excellent straight lines are obtained as indicated by Figures E6 to E9. The volumes V^* used to prepare these figures are given in Tables E1 to E4. Some additional volumes for organic solutes are given in Table E7.

Figures E6 to E9 provide a useful method for interpolation and extrapolation toward providing good estimates of distribution coefficients for those solutes where no experimental data are available.

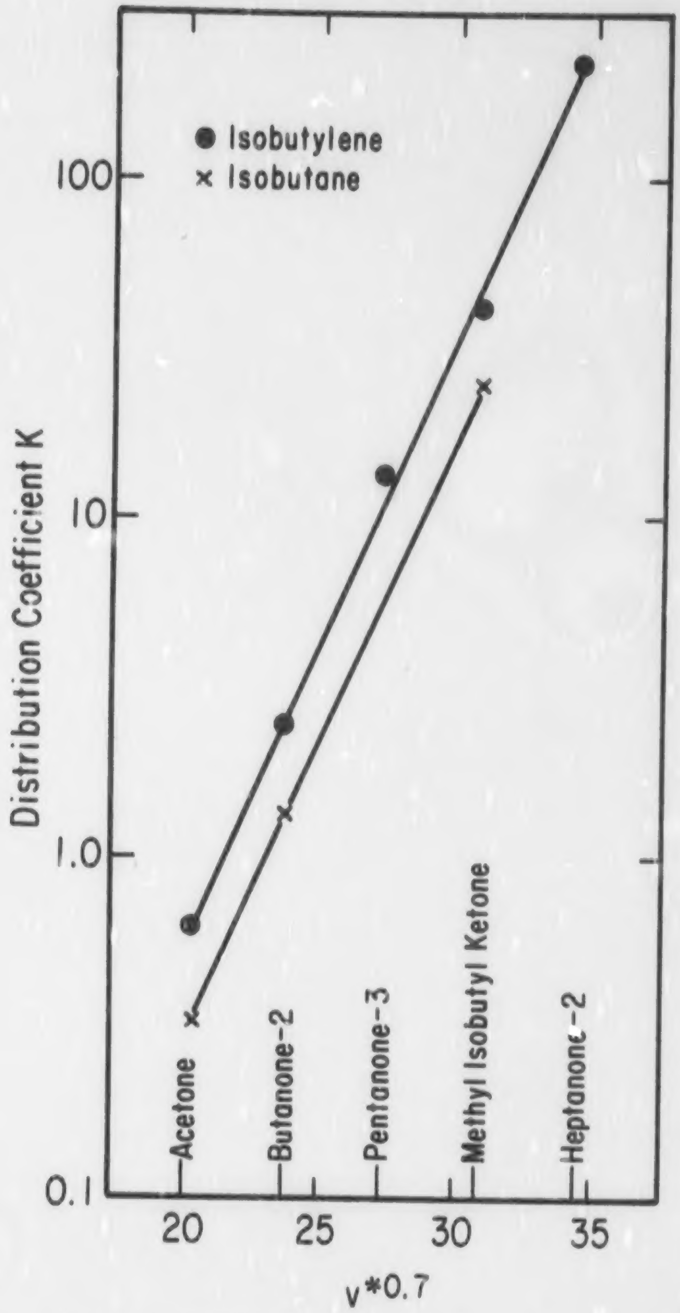
The double bond in crotonaldehyde and the two double bonds in furfuraldehyde tend to lower the distribution coefficient as shown in Figure E8 and in Table E3. However, if the double bond is well removed from the polar functional group, its effect is reduced.

The effect of steric hindrance is evident in Figure E9. When chain branching is close to the polar functional group, the distribution coefficient tends to rise. However, branching well removed from the polar functional group has little influence on the distribution coefficient.



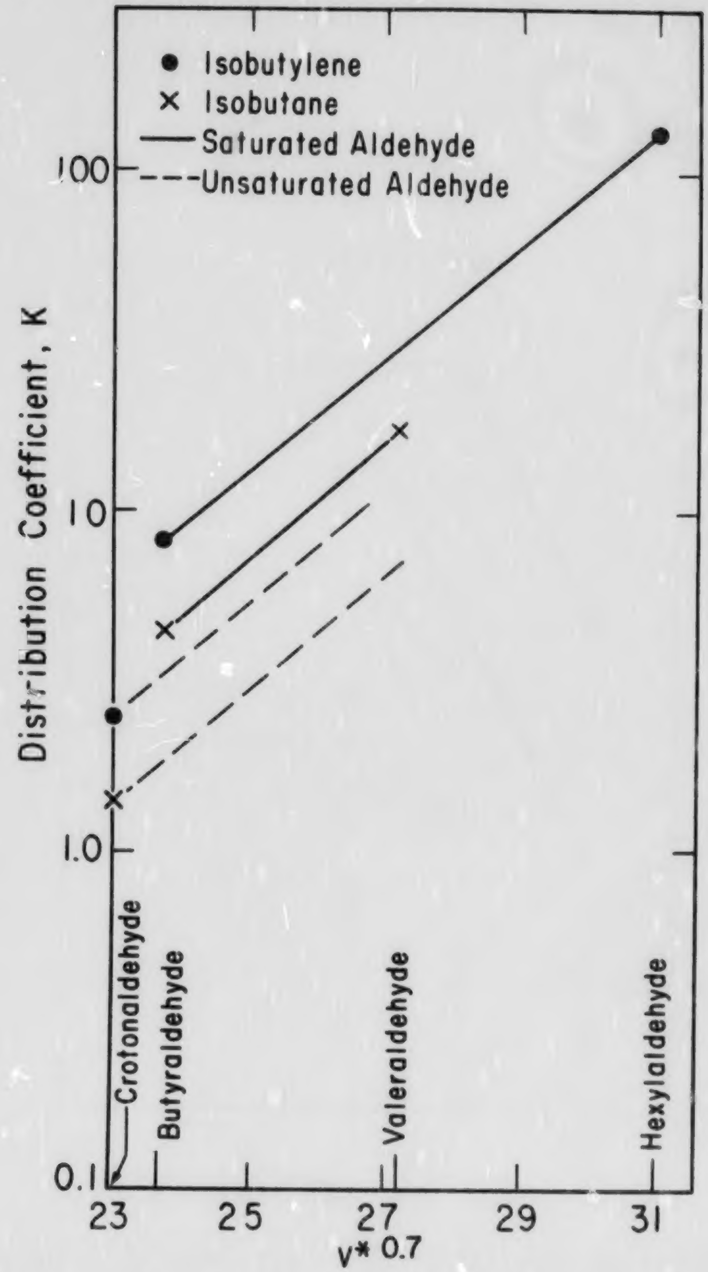
DISTRIBUTION COEFFICIENTS FOR ACETATES BETWEEN WATER AND C_4 HYDROCARBONS AT 25°C

Figure E6



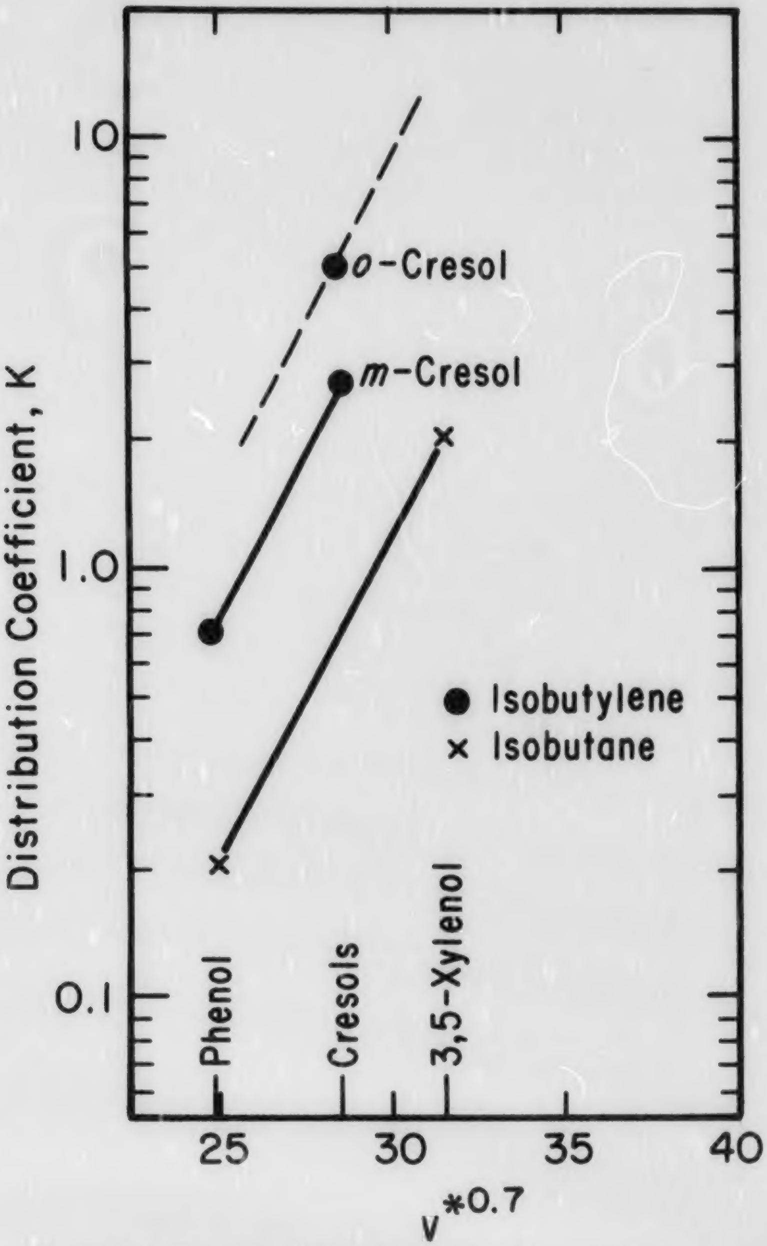
DISTRIBUTION COEFFICIENTS FOR KETONES BETWEEN WATER AND C_4 HYDROCARBONS AT 25°C

Figure E7



DISTRIBUTION COEFFICIENTS FOR ALDEHYDES BETWEEN WATER AND C_4 HYDROCARBONS AT 25 °C

Figure E8



DISTRIBUTION COEFFICIENTS FOR PHENOLICS BETWEEN WATER AND C_4 HYDROCARBONS AT 25°C

Figure E9

Table E6

Constants in Equation (E8) with $q = V^{*0.7}$

	$k/RT, \left(\frac{cm^3}{mole}\right)^{-0.7}$	$-\frac{\Delta U}{RT}$
ISOBUTYLENE		
Acetates	0.387	7.42
Aldehydes	0.41	7.62
Ketones	0.412	8.81
Phenolics	0.34	8.72
ISOBUTANE		
Alkanes	0.41	0.713
Acetates	0.388	7.98
Aldehydes	0.403	8.08
Ketones	0.411	9.45
Phenolics	0.348	10.2
Alcohols‡	0.41	11.27

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‡Estimated from correlation of Pierotti et al., Ind. Eng. Chem. 51 95 (1959)

Table E7

Characteristic Volumes V^* for Some Other Organic Solutes (cm^3/mol)

Benzene	91.2	Resorcinol	103.2
Toluene	112.6	Acetic Acid	61.2
m-Xylene	133.8	n-Propionic Acid	82.3
Aniline	102.6	n-Butyric Acid	103.7
Methanol	41.1	n-Hexanoic Acid	147.7
Ethanol	60.2	n-Octanoic Acid	192.1
n-Propanol	78.7	Benzoic Acid	123.0
n-Pentanol	118.1	Fluoromethane	36.2
n-Octanol	180.2[†]	Chloromethane	47.9
n-Decanol	228.8	Trichloromethane	80.6
Benzyl Alcohol	117.6	Trichlorofluoromethane	87.8
Ethylene Glycol	62.0	Tetrachloromethane	98.6

[†] Liquid density data extrapolated with the Rackett equation.

Evaluation of Size Parameter V^*

The molecular-size parameter V^* is the molar volume of a saturated liquid in a standard state specified by Hildebrand's rule (Hildebrand, 1939). The standard state chosen here is that state where the vapor volume in equilibrium with the saturated liquid is 100 liters per mole. This state is useful because it corresponds to a temperature range where liquid density data are most frequently available.

The liquid volume V^* is determined from vapor-pressure and liquid-density data. The vapor pressure P is represented as a function of temperature T by the Antoine equation

$$\ell n\, P = A - B(C + T)^{-1} \qquad \text{(E9)}$$

where A, B and C are empirical constants. When the vapor volume is 100 liters per mole, the pressure is given by the ideal-gas law

$$P = RT(100)^{-1} \qquad \text{(E10)}$$

Simultaneous solution of Equations (E9) and (E10) fixes the temperature.

The molar liquid volume V is given as a function of temperature by an equation of the Rackett form (Rackett 1970):

$$\ell n\, V = D + E(1 - T/T_c)^{2/7} \qquad (E11)$$

where T_c is the critical temperature and where D and E are empirical constants. When the temperature determined from Equations (E9) and (E10). is substituted into Equation (E11), we obtain the parameter V^* The compilation by Francis (1959) is particularly useful for obtaining constants D and E from density data for organic liquids.

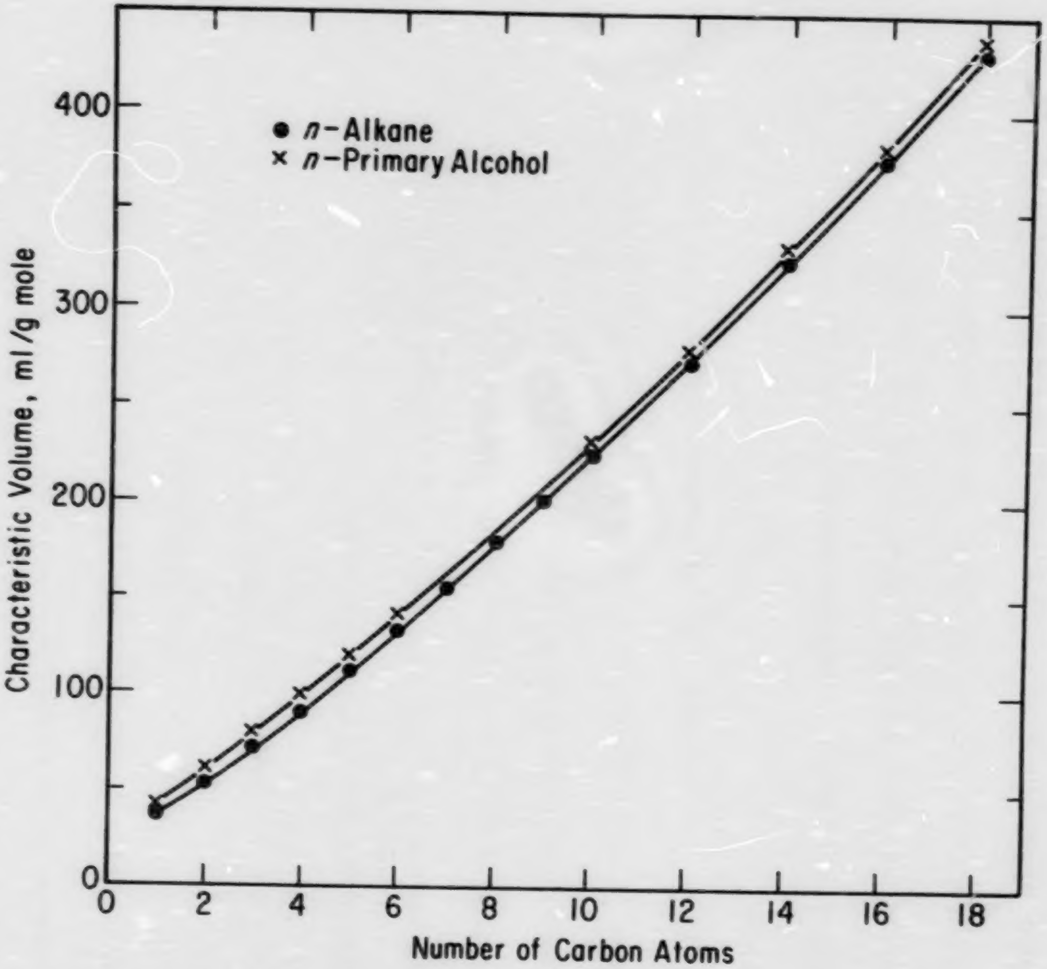
Correlation of Characteristic Volume V^*

To evaluate the characteristic volume V^* for a fluid, liquid-density and vapor-pressure data are needed near the temperature where the saturated vapor of the fluid is 100 liter/mole. For some fluids of interest, such data are often not available. For the majority of polar fluids, the characteristic volume V^* can be estimated with fair accuracy based on that of the parent hydrocarbon containing the same number of carbon atoms.

Figure $\overset{\text{E10}}{/}$ shows the effect of carbon number on the characteristic volume V^* for n-alkanes and primary n-alcohols. The characteristic volumes for n-alkanes and primary n-alcohols, when compared at equal carbon number, differ by a constant. This constant (ΔV^*_g) is a characteristic group volume V^*_g of group g minus that of methylene (or methyl) group or hydrogen atom. For primary n-alkanols,

$$\begin{aligned} \Delta V^*_{OH} &= V^*_{OH} - V^*_{H} \\ &= 6.6 \text{ (ml/mole)} \qquad \text{(E12)} \end{aligned}$$

ΔV^*_g may vary slightly when the molecule contains only one or two carbon atoms; however, for these small molecules, the necessary data are usually available.



EFFECT OF CARBON NUMBER ON THE CHARACTERISTIC VOLUMES FOR *n*-ALKANES AND *n*-PRIMARY ALCOHOLS

Figure E10

Table E8 shows ΔV_g^* for five common polar solvents. Using ΔV_g^* given in Table E8 V^* for a polar fluid is calculated from V^* for parent hydrocarbon by

$$V_{ng}^* = V_n^* + \Delta V_g^* \qquad \text{(E13)}$$

where subscript n refers to a molecule with carbon number n and subscript g refers to a molecule with group g.

Table E9 shows the experimental and calculated V^* for some typical fluids.

Table E8

Relative Characteristic Group Volume, ΔV_G^* for Equation (E13)

Fluid	ΔV_G^* Definition	ml/mole
Aliphatic Alcohol	$V_{OH}^* - V_H^*$	6.6
Aliphatic Ether	V_O^*	9.7
Aliphatic Ketone	$V_{CO}^* - V_{CH_2}^*$	1.4
Aliphatic Acetate Ester	$V_{CO_2}^* - V_{CH_2}^*$	11
Aliphatic Aldehyde	$V_{CHO}^* - V_{CH_3}^*$	1.0

Table E9

Experimental and Calculated V^* for Some Polar Fluids

Fluid	Characteristic Volume , Experimental	V^* (ml/mole) Calculated
Phenol	98	97.8
m-Cresol	119	119.2
3, 5-Xylenol	139	140.2
Resorcinol	103.2	104.4
Benzylalcohol	117.6	119.2
Methyl Propionate	102	99.6
Ethyl Propionate	121.4	122.7
Ethyl Propyl Ether	121.6	121.4

Notation (Appendix E)

A, B, C, D, E = Empirical constants

c = Concentration of solute, $\frac{\text{g mole solute}}{\text{1000 g solvent}}$

$\bar{g}$ = Partial molar Gibbs energy, $\frac{\text{cal}}{\text{mole}}$

k = Proportionality constant

K = Distribution coefficient, $\frac{\text{concentration in organic phase}}{\text{concentration in aqueous phase}}$

P = Vapor pressure

q = Molecular-size parameter

R = Gas constant

$\bar{s}$ = Partial molar entropy, $\frac{\text{cal}}{\text{mole}}$

T = Absolute temperature

$\bar{u}$ = Partial molar internal energy, $\frac{\text{cal}}{\text{mole}}$

U = Characteristic interaction energy, $\frac{\text{cal}}{\text{mole}}$

V = Molar liquid volume, $\frac{\text{cm}^3}{\text{mole}}$

V^* = Characteristic volume, $\frac{\text{cm}^3}{\text{mole}}$

$\bar{v}$ = Partial molar volume, $\frac{\text{cm}^3}{\text{mole}}$

γ = Activity coefficient, $\frac{\text{activity}}{\text{concentration}}$

Subscripts

eq = Equilibrium

c = Critical

Superscripts

0 = Ideal-gas state

' = Aqueous phase

" = Organic phase

m = Exponent

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APPENDIX F

DISTRIBUTION OF PHENOLIC SOLUTES BETWEEN POLAR ORGANIC SOLVENTS AND WATER*

Introduction

Recently, Abrams and Prausnitz(1) presented distribution-coefficient data for phenolics between water and nonpolar hydrocarbon solvents and also gave a correlation of experimental results based on the theory of associated solutions. This Appendix presents distribution-coefficient data for phenolics between water and polar organic solvents. Particular attention is given to the effect of solute concentration on the distribution coefficient. The experimental results are correlated with a theory similar to that used by Abrams but extended to allow for solvation between the phenolic solute and the polar organic solvent

For removal of phenolic solutes from water by extraction, polar organic fluids are much better solvents than nonpolar hydrocarbons; for example, the distribution coefficient for phenol between water and butyl acetate is much larger than that between water and benzene. Unfortunately, however, compared to nonpolar solvents, polar solvents are much more soluble in water. Therefore, while a polar solvent is useful for extraction of phenolic solutes from water, the raffinate water must be treated subsequently to remove the dissolved polar solvent. Such removal is accomplished with high efficiency by volatile-solvent extraction.

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* References and Nomenclature for this Appendix are given at the end of the Appendix.

Experimental

Distribution coefficients for phenol and for other phenolics were determined by measuring equilibrium solute concentrations in the aqueous phase and in the organic phase. Reagent-grade chemicals were used without further purification. About 100 ml each of organic solvent and aqueous solution were equilibrated in a 250 ml Erlenmeyer flask, sealed with a ground-glass top and stirred by a Teflon-coated magnetic stirring bar. Equilibrium was attained after two hours of stirring. Both phases were transferred into a separatory funnel and allowed to settle for two hours prior to separation. Both phases were removed and stored in 50 ml volumetric flasks. Chemical analysis was performed with a Perkin-Elmer model 990 gas chromatograph, equipped with a dual-flame ionization detector. Two stainless-steel columns (1 meter long, 3.18 mm O.D.), packed with Porapak Q, were used with helium as carrier gas. Five-microliter aqueous samples and one-half-microliter organic samples were used to obtain chromatograms. For calibration, standard aqueous and organic samples were prepared such that solute responses in the detector were similar to those of the test samples. Fresh standard samples were prepared frequently because the solute response was not linear with solute concentration and because the sensitivity of the detector varied slightly from day to day. Typically five to six samples were analyzed for each distribution coefficient.

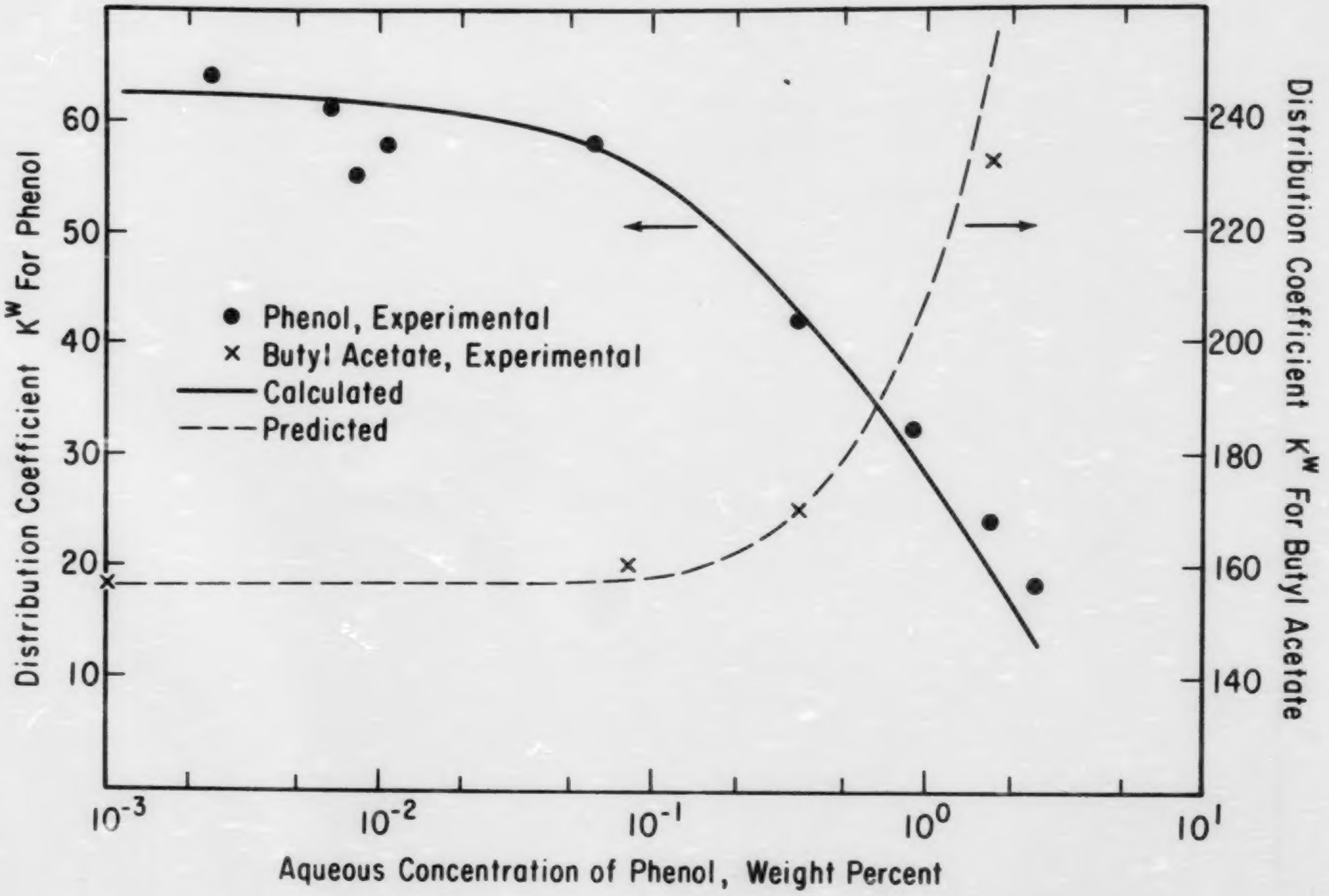
Effect of Solute Concentration

Distribution coefficients in butyl acetate and in methyl isobutyl ketone were measured at high dilution for the following phenolic solutes: phenol, m-cresol, 3,5-xylenol, pyrocatechol, resorcinol, and o-chlorophenol. Results are given in Table F1

The distribution coefficient K^w is defined by

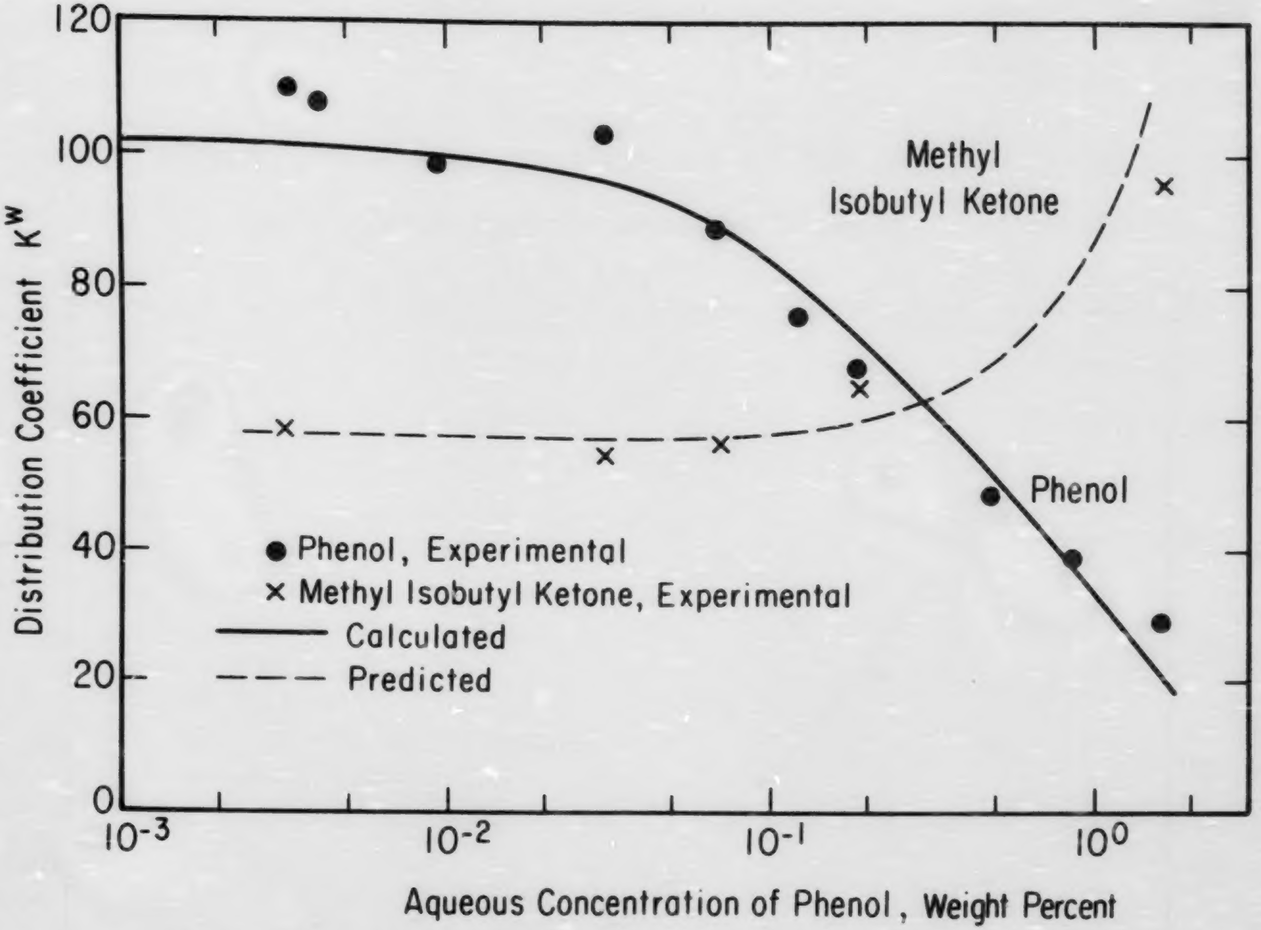
$$K^w = \frac{\text{weight \% solute in water-free solvent}}{\text{weight \% solute in water}} \tag{F1}$$

The effect of solute concentration on the distribution coefficient of phenol was measured for four polar solvents: butyl acetate, methyl isobutyl ketone, isopropyl ether and 1,2-dichloroethane; results are given in Tables F2-F5 and Figures F1-F4. The effect of solute concentration on the distribution coefficient of resorcinol was measured with butyl acetate; results are given in Table F6 and in Figure F5. Tables F2, F3, F4 and F6 also report measured distribution coefficients for the polar organic solvent between water and itself.



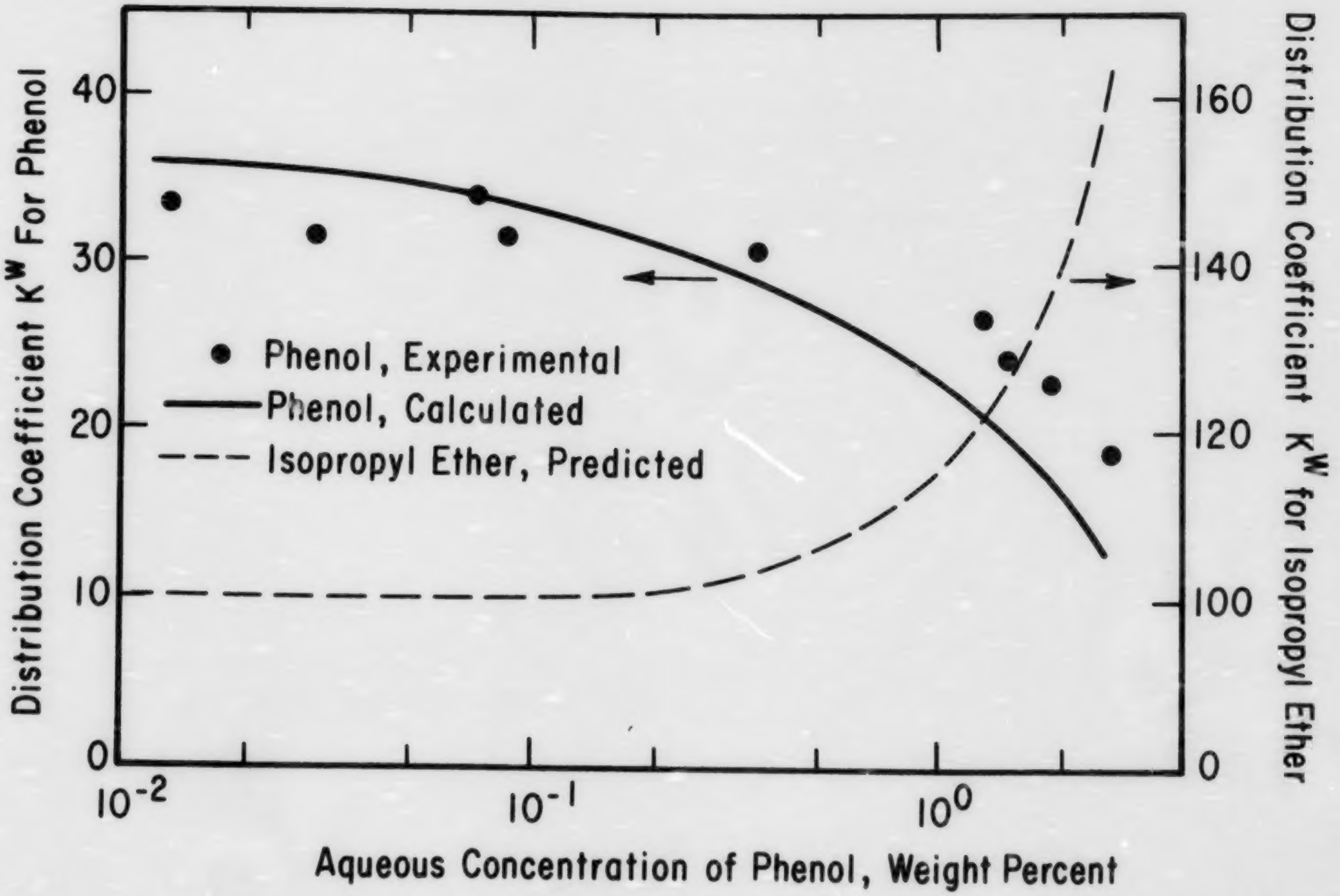
DISTRIBUTION COEFFICIENTS FOR PHENOL AND BUTYL ACETATE
BETWEEN WATER AND BUTYL ACETATE AT 25°C

Figure F1



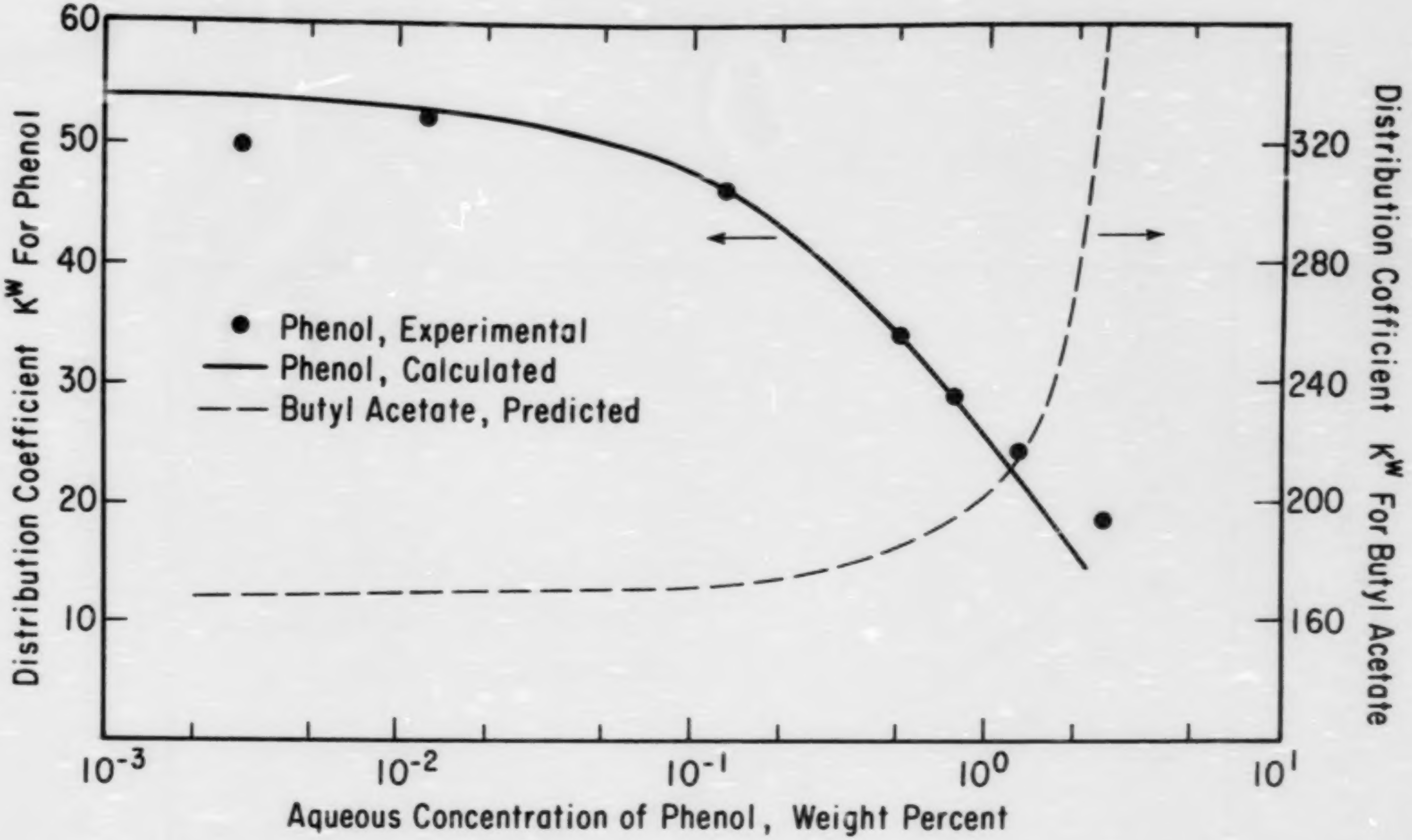
DISTRIBUTION COEFFICIENTS FOR PHENOL AND METHYL ISOBUTYL KETONE BETWEEN WATER AND METHYL ISOBUTYL KETONE AT 25°C

Figure F2



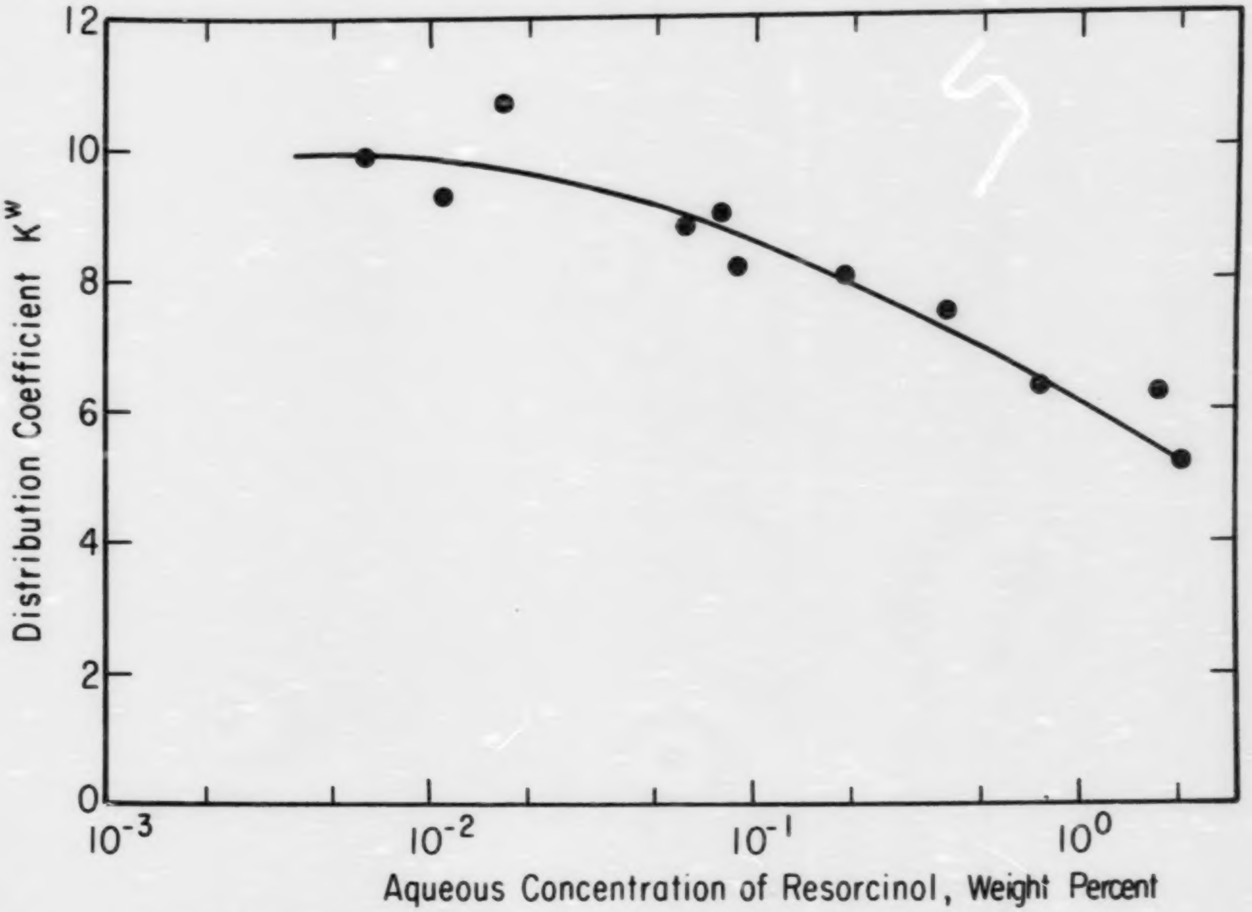
DISTRIBUTION COEFFICIENTS FOR PHENOL AND ISOPROPYL ETHER BETWEEN WATER AND ISOPROPYL ETHER AT 25°C

Figure F3



DISTRIBUTION COEFFICIENTS FOR PHENOL AND BUTYL ACETATE BETWEEN WATER AND BUTYL ACETATE AT 45°C

Figure F4



DISTRIBUTION COEFFICIENTS FOR RESORCINOL BETWEEN
WATER AND BUTYL ACETATE AT 25°C

Figure F5

TABLE F1

Distribution Coefficients for Phenolics Between Water and Two Organic Solvents at High Dilution at 25°C

	Distribution Coefficient, K^W	
Solute	Butyl Acetate	Methyl Isobutyl Ketone
Phenol	65	110
m-Cresol	153	264
3,5-Xylenol	540	814
Pyrocatechol (o-Dihydroxy Phenol)	13.2	20.3
Resorcinol (m-Dihydroxy Phenol)	9.9	15.2
o-Chlorophenol	287	490

TABLE F2

Distribution Coefficients for Phenol and Butyl Acetate Between Water and Butyl Acetate

	Phenol Conc. in Water, wt. %	Distribution Coefficient, K^w	
		Phenol	Butyl Acetate
25°C	0.0025	64	157
	0.007	61	157
	0.0085	55	-
	0.011	58	-
	0.061	58	171
	0.083	56	160
	0.35	42	170
	0.93	32	184
	1.75	24	232
	2.48	19	-
45°C	0.003	50	-
	0.0125	52	-
	0.13	46	-
	0.52	34	-
	0.8	29	-
	1.3	25	-
	2.45	23	-

TABLE F3

Distribution Coefficient for Phenol and Isopropyl Ether Between Water and Isopropyl Ether at 25°C

Phenol Conc. in Water, wt. %	Distribution Coefficient, K^w Phenol	Isopropyl Ether
0.03	32	-
0.013	34	99
0.066	34	108
0.089	32	-
0.36	31	117
0.52	34	-
1.32	27	-
1.55	25.	-
1.92	23	-
2.7	19	-

TABLE F4

Distribution Coefficients for Phenol and Methyl Isobutyl Ketone Between Water and Methyl Isobutyl Ketone at 25°C

Phenol Conc. in Water, wt. %	Distribution Coefficient, K^W Phenol	MIB Ketone
0.0033	110	58
0.0041	108	-
0.0093	99	-
0.031	103	55
0.070	89	56
0.12	76	-
0.19	68	65
0.48	48	-
0.89	39	-
1.64	29	96

TABLE F5

Distribution Coefficients for Phenol Between Water and 1,2-Dichloroethane at 25°C

Phenol Conc. in Water, wt. %	Distribution Coefficient, K^W
0.32	4.1
0.8	4.3
1.7	5.7

TABLE F6

Distribution Coefficients for Resorcinol and Butyl Acetate Between Water and Butyl Acetate at 25°C

Resorcinol Conc. in Water, wt. %	Distribution Coefficient, K^{w}	
	Resorcinol	Butyl Acetate
0.0064	10	-
0.011	9	-
0.017	10	-
0.061	9	150
0.080	9	-
0.19	8	156
0.39	7	-
0.77	6	-
1.75	6	-
2.03	5	-

The precision of the data is approximately ± 5% for aqueous solute concentrations above 200 ppm and approximately ± 7% for aqueous concentrations below 200 ppm. The distribution coefficient data for phenol between water and butyl acetate (and methyl isobutyl ketone) at 25°C agree well at high solute concentrations with those reported by Narasimhan *et al.*(6) however, at low concentrations the results shown in Table F2 for phenol at 25°C are about 20% below those reported by Kiezyk and Mackay(7). At high dilution (aqueous concentration less than 500 ppm) the distribution coefficients for phenol shown in Table F3 are in fair agreement with those of Kiezyk and Mackay(7)

Thermodynamic Analysis

For a phenolic solute (designated by subscript A) distributed between an organic phase (designated by superscript o) and an aqueous phase (designated by superscript a), the distribution coefficient K_A^x is defined by

$$K_A^x = \frac{x_A^o}{x_A^a} = \frac{\gamma_A^a}{\gamma_A^o} \qquad (F2)$$

For a polar solvent (designated by subscript B), the distribution coefficient K_B^x is similarly defined:

$$K_A^x = \frac{x_B^o}{x_B^a} = \frac{\gamma_B^a}{\gamma_B^o} \qquad (F3)$$

where X is the mole fraction and γ is the activity coefficient. The standard state for each component in either phase is the pure liquid at system temperature and pressure. Distribution coefficient K^x is calculated from experimental K^w by

$$K_A{}^x = K_A{}^w \left(\frac{M^o}{M^a}\right) \tag{F4}$$

$$K_B{}^x = K_B{}^w \left(\frac{M^o}{M^a}\right) \tag{F5}$$

where M^a is the average molecular weight of the aqueous phase and M^o is the average molecular weight of the organic phase on a water-free basis.

At equilibrium, the aqueous phase contains a small amount of polar organic solvent. We consider the aqueous phase to be a ternary solution with relatively low concentrations of solute and organic solvent and an excess of water. For the activity coefficients of solute A and organic solvent B in water W, we write two-suffix Margules equations:

$$\ln \gamma_A{}^a = D_{AW}\left(X_W{}^a\right)^2 + D_{AB}\left(X_B{}^a\right)^2 + \left(D_{AW} + D_{AB} - D_{WB}\right) X_B{}^a X_W{}^a \tag{F6}$$

$$\ln \gamma_B{}^a = D_{WB}\left(X_W{}^a\right)^2 + D_{AB}\left(X_A{}^a\right)^2 + \left(D_{WB} + D_{AB} - D_{AW}\right) X_A{}^a X_W{}^a \tag{F7}$$

where D designates the Margules coefficient. At 25°C, Tsonopoulos(8) reports that for phenol D_{AW} is 3.9. Some other Margules coefficients in dilute aqueous solution are given in Table F7.

For γ_A° and γ_B°, we use a theory of associated solutions similar to that given by Renon and Prausnitz(9), based on the model of Kretschmer and Wiebe(10). The key assumptions are:

1. The solute in the organic phase exists in the form of linear, hydrogen-bonded polymers designated by A_1 for monomer, A_2 for dimer, etc. These polymers are in chemical equilibrium

$$A_n + A_1 \rightleftharpoons A_{n+1} \qquad (F8)$$

2. The equilibrium constant κ_e, defined below, is independent of n.

$$\kappa_e = \frac{\phi_{A_{n+1}}}{\phi_{A_n}\phi_{A_1}} \quad \frac{n}{n+1} \qquad (F9)$$

where ϕ is the "true" volume fraction. For a fixed solute, equilibrium constant κ_e is a function only of temperature. It is independent of the organic solvent. Equilibrium constants κ_e for phenolic solutes have been correlated by Abrams and Prausnitz (1).

3. The molar volume of an n-mer is related to that of a monomer by

$$V_{A_n} = nV_{A_1} \qquad (F10)$$

TABLE F7

Margules Constants for the Aqueous Phase [Equations (F6) and (F7)] and Solubilities in Solute-Free Water of Polar Solvents at 25°C

	D_{AB} (1)	D_{WB} (2)	X_B^a (3)
Butyl Acetate	-2.15	7.0	0.94×10^{-3}
Methyl Isobutyl Ketone	-2.5	5.85	2.9×10^{-3}
Isopropyl Ether	-1.37	6.34	1.8×10^{-3}

Subscript W refers to water, A to phenol, and B to polar solvent. Superscript a refers to aqueous phase.

(1) Calculated from

$$D_{AB} = 3.9\,(1 - X_B^{a})^2 - \ln K_A^{\infty x}$$

(2) Calculated from

$$D_{WB} = - \frac{\ln X_B^{a}}{\left(1 - X_B^{a}\right)^2}$$

(3) Measured by authors

4. Interactions between solute polymer A_n and polar organic solvent B are described by the chemical equilibrium

$$A_n + B_1 \rightleftharpoons A_nB_1 \qquad \text{(F11)}$$

5. The equilibrium constant κ_s, defined below, is independent of n.

$$\kappa_s = \frac{\phi_{A_nB_1}}{\phi_{A_n}\phi_{B_1}} \quad \frac{nV_B}{nV_A + V_B} \qquad \text{(F12)}$$

For a given solute, equilibrium constant κ_s is a function of temperature and of the organic solvent.

Following a derivation outlined by Won[2], activity coefficients $\gamma_A{}^{\circ}$ and $\gamma_B{}^{\circ}$ are given by

$$\ell n \gamma_A{}^{\circ} = \ell n \left(\frac{\phi_{A_1}}{X_A \phi^*_{A_1}} \right) + \left(1 - \phi_A - \phi_{B_1} \frac{V_A}{V_B} \right)$$

$$+ \kappa_e \left(\phi_A \phi_{A_1} - \phi^*_{A_1} \right) - \kappa_s \frac{V_A}{V_B} \phi_A \phi_{B_1} \left(1 - \kappa_e \phi_{A_1} \right) \qquad \text{(F13)}$$

$$\ell n \gamma_B{}^{\circ} = \ell n \left(\frac{\phi_{B_1}}{X_B} \right) + \left(1 - \phi_A \frac{V_B}{V_A} - \phi_{B_1} \right)$$

$$+ \kappa_e \phi_A \phi_{A_1} V_B / V_A - \kappa_s \phi_A \phi_{B_1} \left(1 - \kappa_e \phi_{A_1} \right) \qquad \text{(F14)}$$

In these equations, mole fractions X_A and X_B stand for the overall (stochiometric) mole fractions of solute A and solvent B. Similarly ϕ_A and ϕ_B stand for the overall (stoichiometric) volume fractions. The "true" volume fractions of the monomers ϕ_{A_1} and ϕ_{B_1} are found from simultaneous solution of the material-balance equations

$$\phi_A = \sum_{n=1}^{\infty} \phi_{A_n} + V_A \sum_{n=1}^{\infty} n\phi_{A_nB_1} \Big/ \left(nV_A + V_B\right)$$

$$= \left(1 + \kappa_s \phi_{B_1} V_A/V_B\right) \phi_{A_1} \Big/ \left(1 - \kappa_e \phi_{A_1}\right)^2 \qquad \text{(F15)}$$

$$\phi_B = \phi_{B_1} + V_B \sum_{n=1}^{\infty} \phi_{A_nB_1} \Big/ \left(nV_A + V_B\right)$$

$$= 1 - \phi_A = \phi_{B_1}\left(1 + \frac{\kappa_s \phi_{A_1}}{1 - \kappa_e \phi_{A_1}}\right) \qquad \text{(F16)}$$

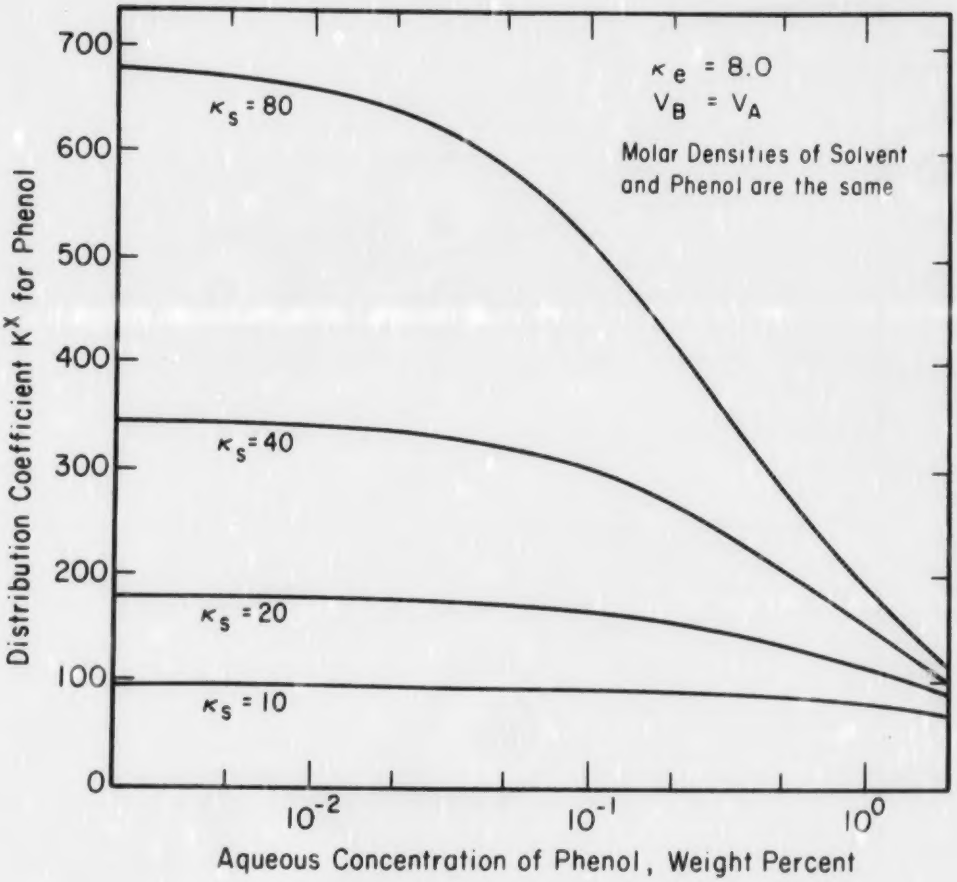
The "true" volume fraction of monomer in the pure state, designated by $\phi_{A_1}^{*}$, is given by

$$\phi_{A_1}^{*} = \lim_{x_B \to 0} \phi_{A_1} = \frac{1 + 2\kappa_e - \sqrt{1 + 4\kappa_e}}{2\kappa_e^{2}} \qquad \text{(F17)}$$

The theory outlined above is similiar to that presented earlier(1,9) in the sense that both theories consider the solute to form linear hydrogen-bonded polymers which are in chemical equilibrium. However, whereas the earlier theory, applicable to solutions in nonpolar solvents, describes solute-solvent interactions with a van Laar term containing a physical parameter β, the present treatment, applicable to solutions in polar solvents, describes solute-solvent interactions in terms of a chemical equilibrium constant κ_s. Similar chemical theories were proposed previously for solutions containing alcohols(4,5).

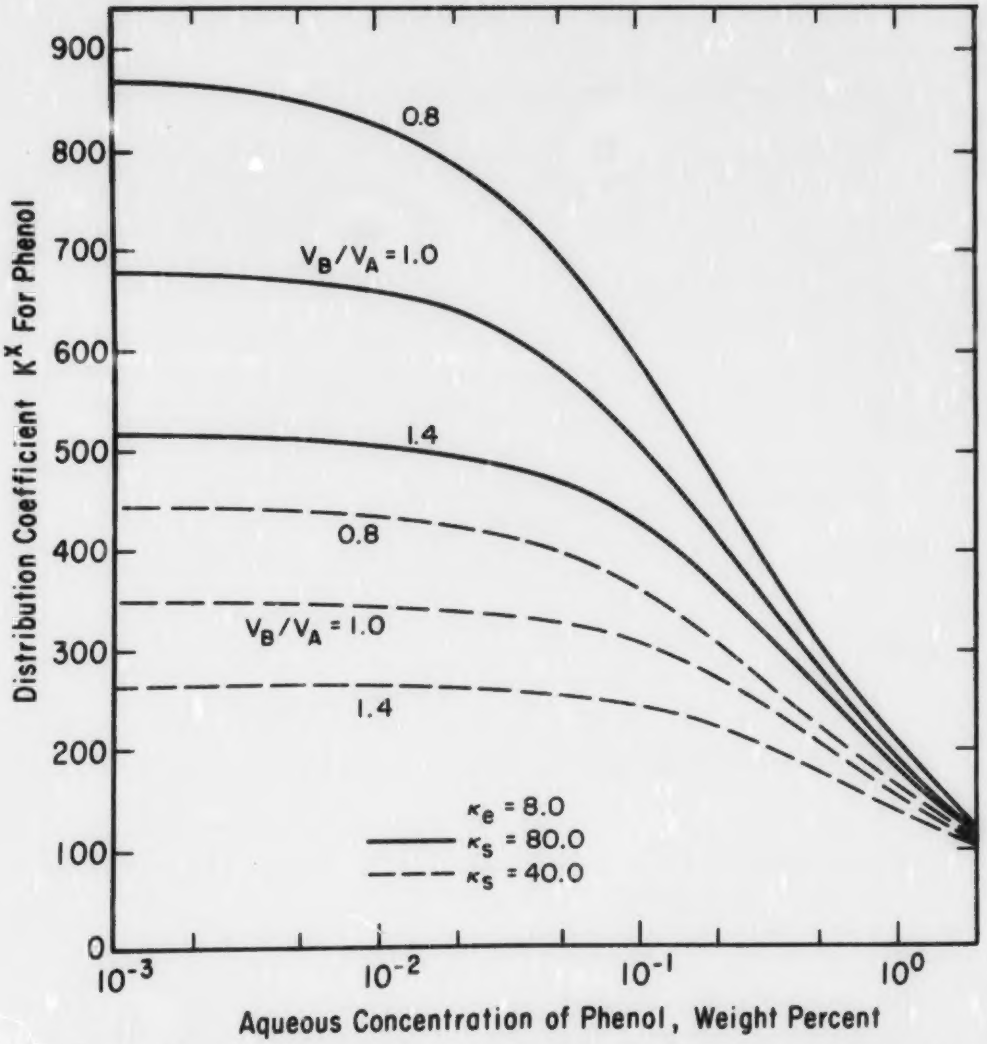
We now consider some results obtained from the thermodynamic analysis; these are given in Figures $\overset{F6}{/}$ and $\overset{F7}{/}$ The calculations shown pertain to phenol near 25°C; we have used $D_{AW} = 3.9$ and for simplicity we have set $X_B^a = 0$.

Figures $\overset{F6}{/}$ and $\overset{F7}{/}$ show how the distribution coefficient for phenol varies with aqueous phenol concentration, solvation equilibrium constant, κ_s and molar volume ratio, V_B/V_A, where B stands for solvent and A for phenol. For large κ_s, the distribution coefficient falls rapidly as the aqueous concentration of phenol rises. For intermediate values of κ_s (about 10), the distribution coefficient is insensitive to aqueous phenol concentration. Although not shown in Figures $\overset{F6}{/}$ and $\overset{F7}{/}$ for small values of κ_s, the distribution coefficient rises slightly with aqueous phenol concentration, consistent with the physical theory (for $\beta < 0$) discussed earlier(1). The chemical theory and the physical theory become identical



EFFECT OF SOLVATION EQUILIBRIUM CONSTANT, κ_s, AND THAT OF AQUEOUS CONCENTRATION ON DISTRIBUTION COEFFICIENTS FOR PHENOL AT 25°C

Figure F6



EFFECT OF AQUEOUS PHENOL CONCENTRATION AND THAT OF VOLUME RATIO (V_B/V_A) ON DISTRIBUTION COEFFICIENTS FOR PHENOL AT 25°C

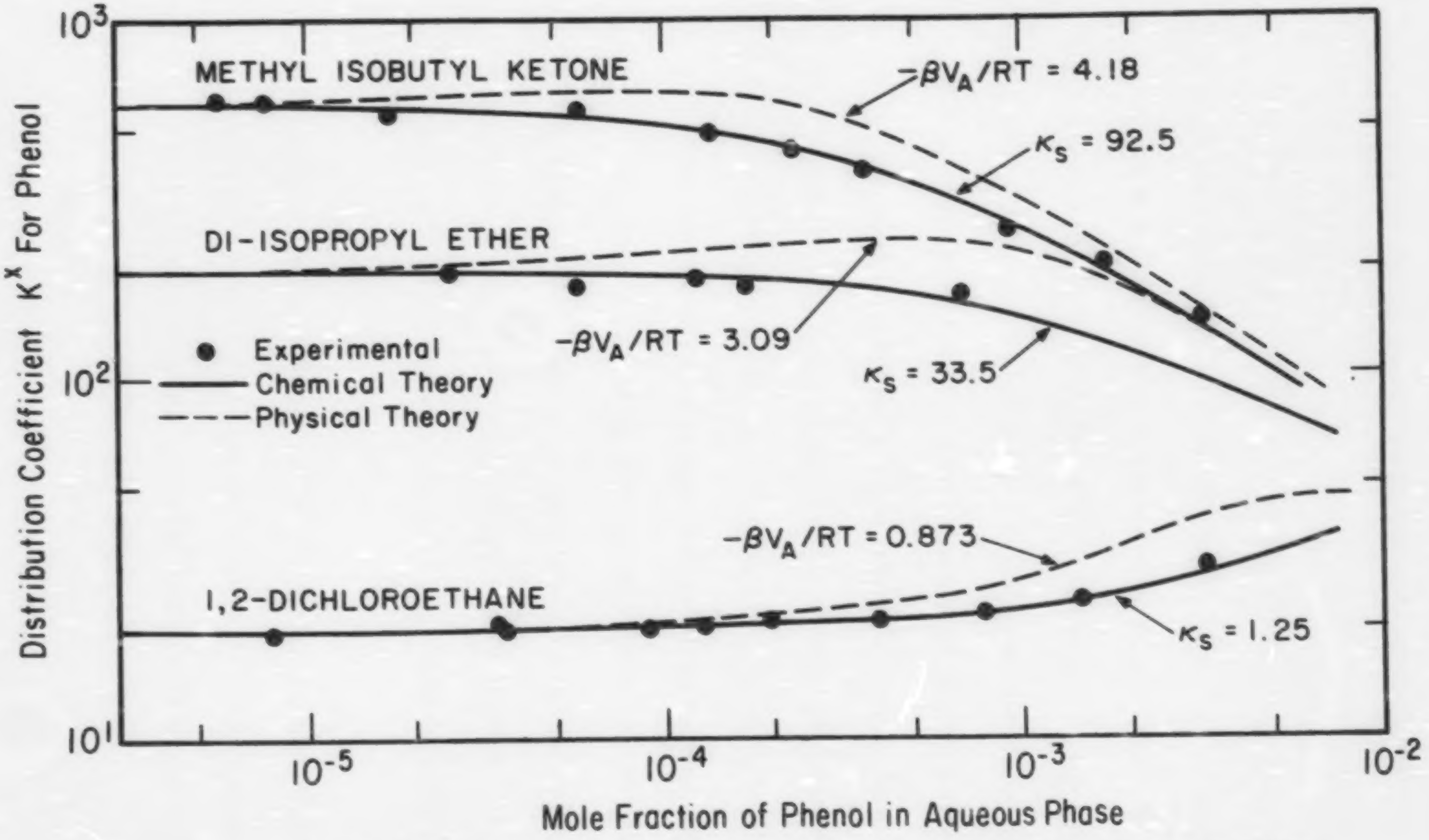
Figure F7

in the limit, as $\kappa_s \rightarrow 0$ in the chemical theory and as $\beta \rightarrow 0$ in the physical theory.

A comparison of the two theories is given in Figure F8. / Calculations were performed for phenol with three solvents. Using experimental distribution-coefficient data at very low phenol concentrations, parameter κ_s (chemical theory) and parameter β (physical theory) were determined as briefly discussed in the next section. Using these parameters, distribution coefficients were then calculated for phenol at higher concentrations.

The results given in Figure F8 / show that a physical theory is adequate only when the attraction between phenol and solvent (negative β) is weak. If that attraction is strong (large κ_s), the chemical theory is required to represent the data over an appreciable concentration range. On the other hand, the chemical theory is not suitable for physical solvents which have little tendency to attract phenol. For such solvents β is positive and therefore the chemical theory does not apply. In Figure F8 /, experimental data for 1,2-dichloroethane at high dilution were taken from Kiezyk and Mackay(7)

To illustrate the applicability of the chemical theory, consider the distribution coefficient for phenol between water and diethyl ketone. Distribution coefficient data at high dilution, reported by Kiezyk and



CONCENTRATION DEPENDENCE OF DISTRIBUTION COEFFICIENTS FOR PHENOL AT 25°C. PREDICTIONS BY CHEMICAL THEORY AND BY PHYSICAL THEORY

Figure F8

Mackay(7), were used to find κ_s. Distribution coefficients at higher phenol concentrations were then predicted as shown in Figure F9. The predictions by chemical theory are in good agreement with experiment(7), considering the large experimental scatter.

Distribution Coefficient at High Dilution

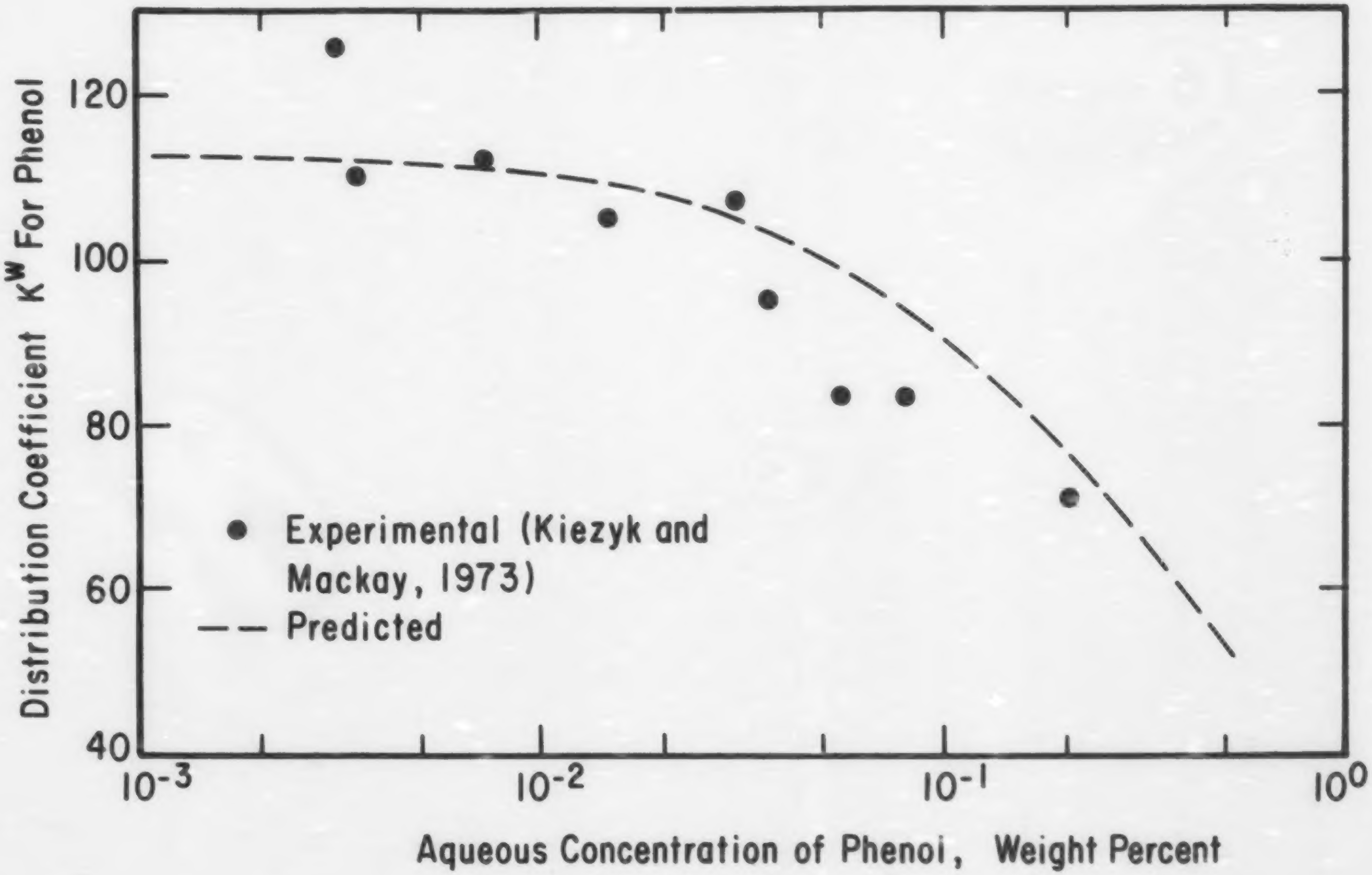
In the limit as $X_A \rightarrow 0$, the thermodynamic equations simplify greatly. In that limit

$$\gamma_A^{\infty o} = \lim_{X_A \rightarrow 0} \gamma_A^{o} = \frac{\exp\left[1 - \frac{V_A}{V_B} - \kappa_e \Phi^*_{A_1}\right]}{\left(\kappa_s + \frac{V_B}{V_A}\right)\Phi^*_{A_1}} \qquad \text{(F18)}$$

$$K_A^{\infty x} = \lim_{X_A \rightarrow 0} K_A^{x} = \frac{\gamma_A^{\infty a}\left[\kappa_s + \frac{V_B}{V_A}\right]\Phi^*_{A_1}}{\exp\left[1 - \frac{V_A}{V_B} - \kappa_e \Phi^*_{A_1}\right]} \qquad \text{(F19)}$$

For phenol at 25°C, $\kappa_e = 8.0$, $\Phi^*_{A_1} = 0.089$ and $\gamma_A^{\infty a}$ is obtained from Equation (F6) with $X_A^{a} = 0$.

In the limit as $X_A \rightarrow 0$, the activity coefficient $\gamma_A^{\infty o}$ according to the physical theory is



EXPERIMENTAL AND PREDICTED DISTRIBUTION COEFFICIENT FOR PHENOL BETWEEN WATER AND DIETHYL KETONE AT 25°C

Figure F9

$$\gamma_A^{\infty o} = \frac{\exp\left[1 - {}^{V_A}\!/\!{}_{V_B} - \kappa_e \phi^*_{A_1} + \beta \frac{V_A}{RT}\right]}{\frac{V_B}{V_A} \phi^*_{A_1}} \tag{F20}$$

Comparing Equations (F18) and (F20) we find

$$\kappa_s \frac{V_A}{V_B} = \exp\left(- \frac{\beta V_A}{RT}\right) - 1 \tag{F21}$$

When

$$\frac{\beta V_A}{RT} \longrightarrow 0 \tag{F22}$$

$$\kappa_s \frac{V_A}{V_B} = - \frac{\beta V_A}{RT} \tag{F23}$$

For small κ_s, and at high dilution, the physical theory (with negative β) gives essentially the same results as the chemical theory, as indicated in Figure F8.

Additional Solvents

Table F8 shows distribution coefficients for phenol between water and thirteen polar organic solvents. The distribution coefficient K^w is defined by Equation F1.

Since the concentrations of phenol in both phases are very small, the experimental distribution coefficients are essentially those corresponding to high dilution. The precision of the data is approximately ± 5%.

Thermodynamic Relations

A thermodynamic distribution coefficient K^x for phenol between the aqueous phase (designated by superscript a) and an organic solvent (designated by superscript s) is defined by

$$K^x = \frac{X^o}{X^a} = \frac{\gamma^a}{\gamma^o} \qquad \text{(F24)}$$

where X is the mole fraction, and γ is the activity coefficient of phenol.

For dilute solutions, distribution coefficient K^x is related to distribution coefficient K^w by

$$K^x = K^w \left(\frac{M^o}{M^a} \right) \qquad \text{(F25)}$$

Table F8

Distribution Coefficients for Phenol at High Dilution Between Water and Polar Solvent at 25°C

Solvent	Aqueous Phenol Conc. wt. %	Distribution Coefficient, K^x	Purity of Solvent
n-Pentanol	0.016	54	Boiling point 136-138°C (MCB)†
n-Decanol	0.029	33	Melting point 5.5-6.5°C (MCB)
Methyl Isobutyl Ketone	0.003	110	Boiling point 114-117°C (MCB)
Octanone-2	0.015	99	Refractive Index $n_D^{20} = 1.4151$ (Aldrich)
Ethyl Acetate	0.018	65	98 + Mole % (MCB)
n-Butyl Acetate	0.003	64	Boiling point 124-126°C (MCB)
Di-Ethyl Ether	0.016	52	Analytical Reagent (Mallinckrodt)
Di-Isopropyl Ether	0.013	34	Boiling point 67-69°C (MCB)

†- Stands for Matheson, Coleman and Bell

Table F8 (continued)

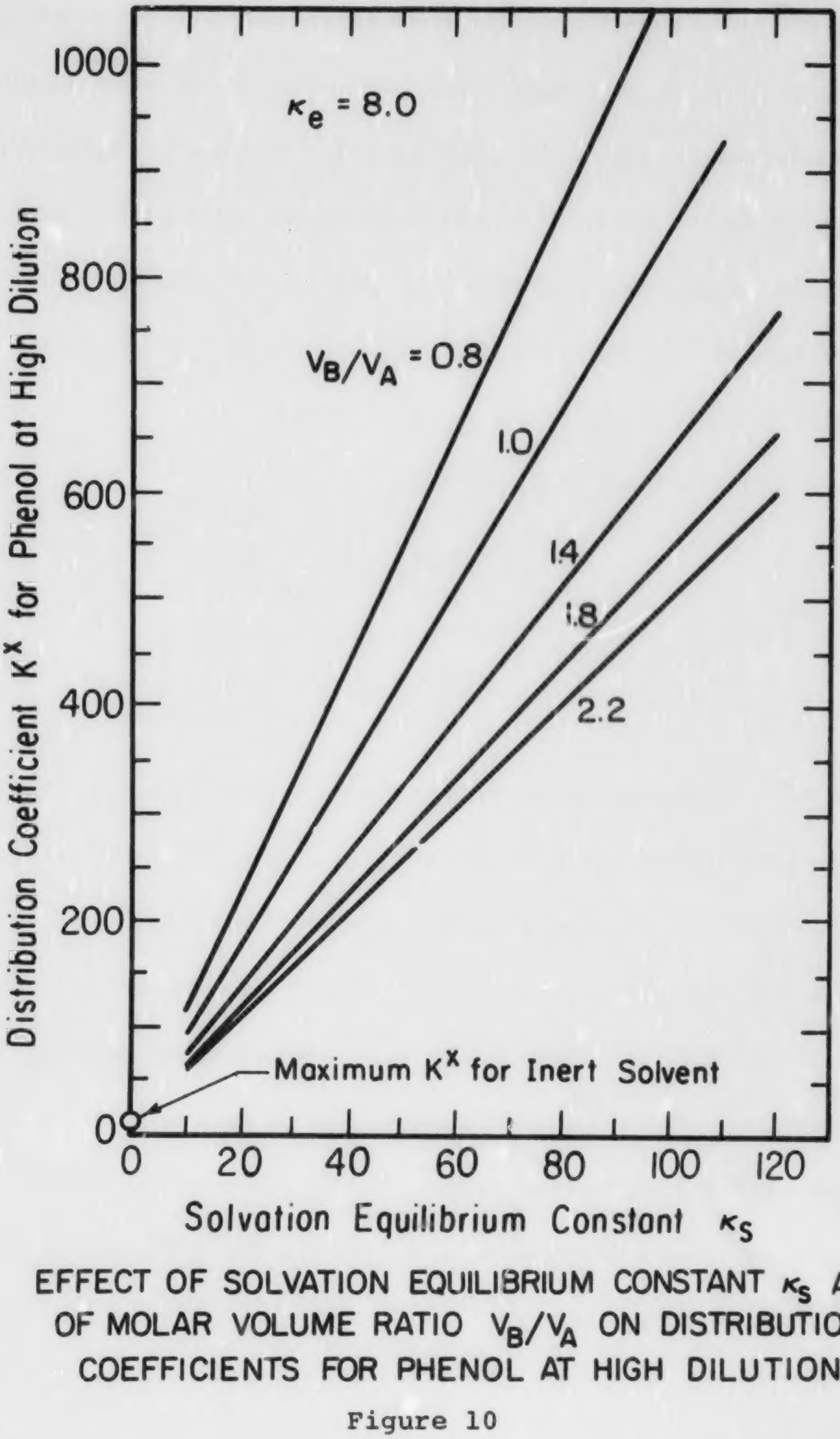
Solvent	Aqueous Phenol Conc. wt. %	Distribution Coefficient, K^x	Purity of Solvent
Di-n-Butyl Ether	0.01	16	Boiling point 140-142°C (MCB)
Nitroethane	0.14	14	Boiling point 112-114°C (MCB)
Valeraldehyde	0.035	59	Boiling point 100-104°C (MCB)
Di-n-Propylamine	0.18	6.7	Refractive Index $n_D^{20} = 1.4051$ (Aldrich)
1,2-Dichloroethane	0.32	4.1	Boiling point 82.7-84.2 °C (MCB)

where M^o is the molecular weight of the solvent and M^a is the average molecular weight of the aqueous phase. According to the chemical theory of liquid solutions distribution coefficient K^x for phenol between water and a polar organic solvent is related to the aqueous mole fraction of phenol X^a, to phenol association equilibrium constant κ_e, to solvation equilibrium constant κ_s, and to the molar volume ratio $\left(V_A/V_B\right)$, where subscript A refers to phenol and B to the solvent.

At high dilution, the relation is

$$K^{\infty x} = \lim_{X_A \to 0} K^x = \frac{\gamma^{\infty a}\left(\kappa_s + V_B/V_A\right)\Phi^*_{A_1}}{\exp\left(1 - \frac{V_A}{V_B} - \kappa_e \Phi^*_{A_1}\right)} \qquad (F26)$$

where $\gamma^{\infty a}$ is the activity coefficient of phenol (referred to pure liquid phenol) in the aqueous phase at high dilution. Near 25°C, $\gamma^{\infty a}$ is 47.3 (8) κ_e is 8.0 (1), the volume fraction of phenol monomer in pure liquid phenol, designated by $\Phi^*_{A_1}$, is 0.089. Figure F10 shows the effect of solvation equilibrium constant κ_s on $K^{\infty x}$ for several values of V_B/V_A. For comparison, Figure F10 also indicates the distribution coefficient obtained with an inert non-polar solvent, where $\kappa_s = 0$. When the solubility of polar solvent in water is appreciable, a correction for $\gamma^{\infty a}$ may be necessary as described above.



EFFECT OF SOLVATION EQUILIBRIUM CONSTANT κ_s AND OF MOLAR VOLUME RATIO V_B/V_A ON DISTRIBUTION COEFFICIENTS FOR PHENOL AT HIGH DILUTION

Figure 10

Table F9 shows density, solubility in water, distribution coefficient for phenol, solvation equilibrium constant and normal boiling point for twenty-two polar solvents. To be useful as an extractant, the density of the solvent should differ from that of water by about 0.1 g/ml; the solubility of the solvent in solute-free water should be small (less than about 2 weight percent) and the distribution coefficient for phenol should be large. For regeneration of the solvent from the phenolic solute, the normal boiling point of the solvent should be well below that of phenol (181.4°C).

Considering the four criteria described above, methyl isobutyl ketone, butyl acetate and diisopropyl ether are potentially good solvents. Aldehydes can not be recommended because of their odor and pentyl (or heavier) alcohols may be difficult to regenerate from phenolics because of their high boiling points.

Data Correlation

Solvation equilibrium constant κ_s is found from experimental values of $K^{\infty x}$ as indicated by Equation F26 These equilibrium constants are plotted against the molar volume ratio V_B/V_A as shown in Figure F11. The data suggest that there is a linear relation for each of three types of polar solvent. The data for isomeric decanols show considerable deviation, probably because of branching near the hydroxyl group. Such branching offers steric hindrance for solvation and lowers κ_s.

Table F9

Properties of Polar Solvents: Density, Solubility in Water, Distribution Coefficient for Phenol, $K^{\infty x}$ and Solvation Equilibrium Constant, κ_s

Solvent	Density (g/ml)	Solubility[‡] in Water (Weight %)	Distribution[‡‡] Coefficient of Phenol, $K^{\infty x}$	Solvation Equilibrium Constant, κ_s	Normal Boiling Point (°C)
Benzyl Alcohol	1.04	4(17)	196 (7)	27	205
n-Pentanol	0.82	2.6	296	45	138
Methyl Cyclohexanol	0.91- 0.94	0.9	352 (7)	55	155- 173
n-Hexanol	0.82	0.6(20)	345 (7)	54	157
n-Octanol	0.83	0.054	348 (7)	63	195
n-Decanol	0.83	(0.004)	298	60	233
Cyclohexanone	0.95	5.0(30)	434 (7)	63	156
Diethyl Ketone	0.82	4.7(20)	554 (7)	82	102
Acetophenone	1.03	0.54	514 (7)	77	202
Methyl Isobutyl Ketone	0.8	1.6	611	96	117
Octanone-2	0.82	(0.1)	704	126	173
Ethyl Acetate	0.90	8.8	318	45	77

F9

Table / (continued)

Solvent	Density (g/ml)	Solubility[‡] in Water (Weight %)	Distribution[‡‡] Coefficient of Phenol, $K^{\infty x}$	Solvation Equilibrium Constant, κ_s	Normal Boiling Point (°C)
n-Butyl Acetate	0.88	0.6	413	66	127
Benzyl Acetate	1.06	$4^{(17)}$	196 (7)	26	214
n-Octyl Acetate	0.89	(0.01)	514 (7)	103	210
Di-Ethyl Ether	0.71	$75^{(20)}$	230	34	35
Di-Isopropyl Ether	0.81	0.95	193	32	68
Di-n-Butyl Ether	0.77	(0.06)	106	20	142
Valeralde-hyde	0.82	-	282	39	103
Di-n-Propylamine	0.74	2.5	37	5.3	110
Nitro-ethane	1.04	4.7	57	4.5	115
1,2-Dichloro Ethane	1.26	0.9	19	1.1	84

[‡] At 25°C, unless otherwise specified, Superscript number in parentheses indicates temperature where the solubility is measured. Number in parentheses indicates estimated solubility.

[‡‡] Experimental data from this research unless otherwise specified. Superscript number in parentheses indicates data source.

Figure F11 indicates that to a good approximation

$$\kappa_s = \hat{\kappa}_s \frac{V_B}{V_A} \qquad \text{(F27)}$$

where $\hat{\kappa}_s$ is the slope of the lines shown in Figure F11.

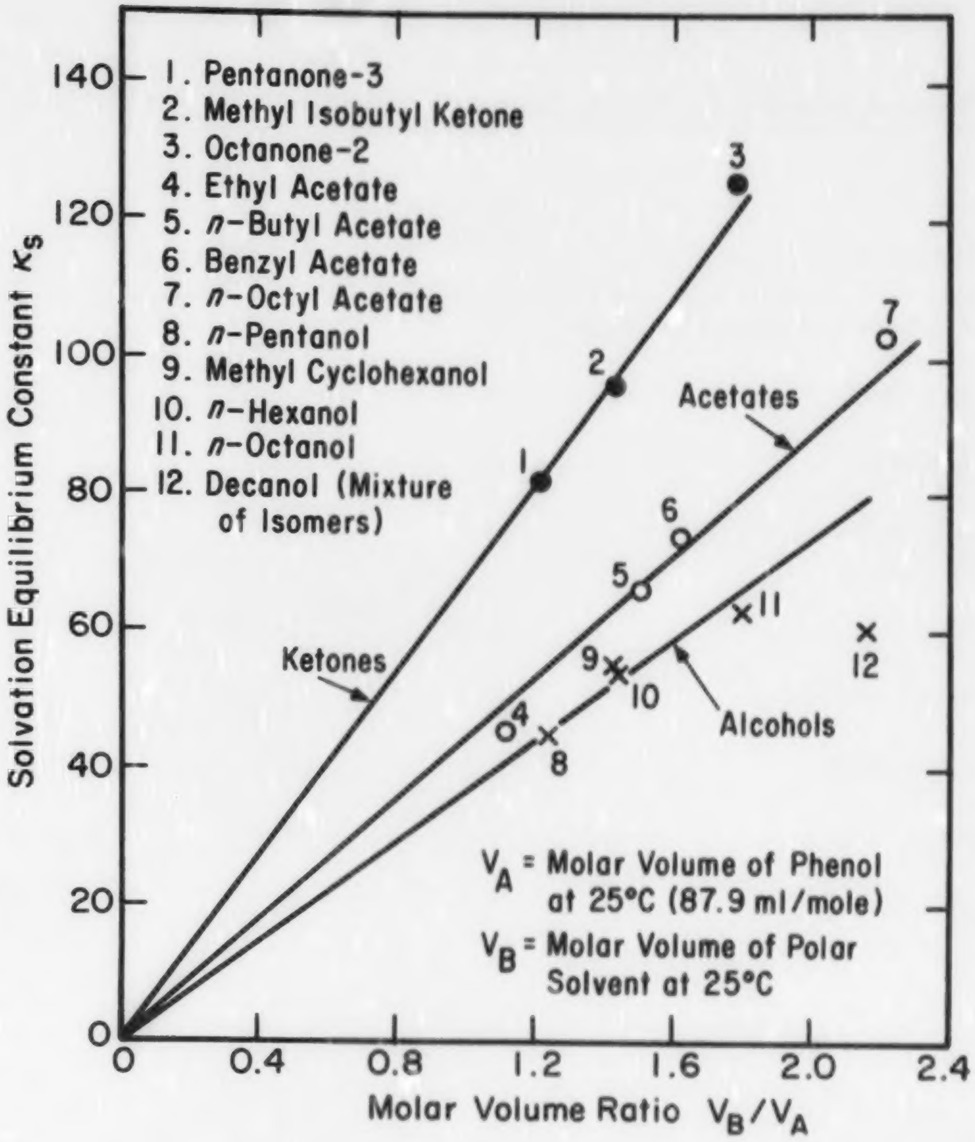
It appears that the reduced solvation equilibrium constant $\hat{\kappa}_s$ depends only on the type of polar solvent. According to the chemical theory of solutions the reduced solvation equilibrium constant $\hat{\kappa}_s$ is related to Δg^s, the standard Gibbs energy of complex formation between phenol and polar solvent, by

$$\ln\left(\kappa_s \frac{V_B}{V_A}\right) = \ln \hat{\kappa}_s = -\frac{\Delta g^s}{RT} + \ln(\tau - 1) \qquad \text{(F28)}$$

where τ is the coordination number, a constant, here taken as 10.

Table F10 shows the reduced solvation equilibrium constant, and the standard Gibbs energy change Δg^s for complex formation between the hydroxyl group in phenol and the polar functional group in the solvent. Large negative values of Δg^s indicate strong affinity between these groups.

The simple relation given by Equation F27 holds for a homologous series, that is, for a series where the polar functional group is freely exposed and not sterically hindered. For example, Equation F27 does not hold for dialkyl ethers because the ether group is increasingly shielded as molecular size increases.



EFFECT OF MOLAR VOLUME OF POLAR SOLVENT ON THE SOLVATION EQUILIBRIUM CONSTANT κ_S FOR PHENOL

Figure F11

TABLE F10

Reduced Solvation Equilibrium Constant $\hat{\kappa}_s$ for Nine Types of Polar Solvents

Polar Solvent Type	$\hat{\kappa}_s$	Δg^s $\frac{\text{Kcal}}{\text{mole}}$
Aliphatic and Aromatic Ketone	63	-1.15
Naphthenic Ketone	50	-1.01
Acetate	45	-0.95
Aliphatic and Naphthenic Alcohols	33	-0.77
Aldehyde	32	-0.75
Aromatic Alcohol	22	-0.53
Nitroparaffin	5.3	+0.31
Dialkyl Amine	3.4	+0.57
Dichloroparaffin ‡	1.1	+1.24

‡ Two chlorines attached to two different carbons

Distribution Coefficients for Phenol Derivatives

At high dilution, the distribution coefficient $K_i^{\infty x}$ for phenolic derivative i between water and organic solvent, can be related to that for phenol $K_A^{\infty x}$ between water and the same solvent by an expression of the form

$$\ell n\, K_i^{\infty x} = \ell n\, K_A^{\infty x} + \sum_j \nu_j\, \ell n\, K_j^{\infty x} \qquad \text{(F29)}$$

where subscript A refers to phenol, and subscript j refers to any group in the meta or para position on the aromatic ring. The number of groups of type j is designated by ν_j and $K_j^{\infty x}$ is the "group distribution coefficient" for group j.

Table F11 shows the logarithms of the group distribution coefficients for methyl, hydroxyl and chlorine groups calculated by Equation F29 from experimental data given above. For comparison, Table F11 also shows the logarithms of group distribution coefficients $K_j^{\infty x}$ for the methyl group between water and six polar solvents (and three non-polar solvents) calculated by analytical-solution-of-groups (ASOG) theory (3). According to the experimental results and ASOG theory, the group distribution coefficient shows appreciable dependence on whether the solvent is polar or non-polar; however, the dependence is insignificant among six polar solvents and among three non-polar solvents as shown in Table F11.

TABLE F11

Calculation of Distribution Coefficients for Phenol Derivatives: Group Contribution, $\ln K_i^{\infty x}$ for Methyl, Chlorine and Hydroxyl Groups near 25°C

Solvent		Groups[‡]			
		Methyl (or Methylene) Experimental	Calculated by ASOG[‡‡]	Chlorine Experimental	Hydroxyl Experimental
Polar Solvent	Butyl Acetate	1.06	1.14	1.20	-1.89
	Amyl Acetate		1.15		
	Hexyl Acetate		1.16		
	Methyl Isobutyl Ketone	1.00	1.09	1.21	-1.98
	Heptanone-2		1.15		
	Octanone-2		1.17		
	Average	1.03	1.14	1.21	-1.95
Nonpolar Solvent	Benzene	1.31	1.33		
	Isobutylene	1.35	1.32		
	Isobutane	1.19	1.31		
	Average	1.25	1.32		

[‡] When the group is located at the ortho position, a steric correction is necessary. Add to Equation 8:

$$\ln K_{ortho}^{\infty x} = \begin{array}{ll} 0.3 & \text{for polar solvents} \\ 0.7 & \text{for nonpolar solvents} \end{array}$$

[‡‡] Parameters for ASOG method obtained from paraffin-water correlation (2) and from paraffin-polar solvent data (9). The differences between experimental and calculated $\ln K_{CH_2}^{\infty x}$ show that there is a difference between the methylene group in paraffins and that in phenolics.

Distribution coefficients for phenol $K_j^{\infty x}$ between water and non-polar solvents were reported above. To estimate the distribution coefficient for phenol between water and a polar solvent, obtain solvation equilibrium constant κ_s for that solvent by Equation F27 and Table F10. With the solvation equilibrium constant κ_s and the molar volume of the solvent V_B, the distribution coefficient for phenol can be estimated from Figure F11. For a phenolic derivative distributed between water and a polar solvent, the distribution coefficient at high dilution can be estimated from that for phenol by Equation F29. Logarithms of group distribution coefficients $K_j^{\infty x}$ are given in Table F11.

Nomenclature

C = concentration, weight percent

Δg^s = Gibbs energy for complex formation, $\frac{\text{Kcal}}{\text{mole}}$

K^w = Distribution coefficient,

$$\frac{\text{weight percent phenol in solvent, water-free basis}}{\text{weight percent phenol in water}}$$

K^x = Distribution coefficient,

$$\frac{\text{mole fraction phenol in solvent}}{\text{mole fraction phenol in water}}$$

V = molar liquid volume, $\frac{\text{ml}}{\text{mole}}$

X = mole fraction

M = molecular weight

Greek Letters

τ = coordination number

$\hat{\kappa}_s$ = reduced solvation equilibrium constant

γ = activity coefficient

κ_e = association equilibrium constant

κ_s = solvation equilibrium constant

$\Phi_{A_1}^*$ = volume fraction of monomeric phenol in pure liquid

ν_j = numer of group j

Superscripts

∞ = at high dilution
s = standard state
o = solvent phase
r = reference sample
a = aqueous phase

Subscripts

A = phenol
i = phenol derivative
B = solvent

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APPENDIX G

EXPERIMENTAL DATA FROM SPRAY COLUMN EXTRACTOR

The data which were directly measured at steady state in each run conducted in the spray column included the solvent and water flow rates, the temperatures of the two streams leaving the extractor, and the concentrations of each solute in the feed and product water. Since the difference between the two temperature measurements was always less than 1°C, the average was taken as the column temperature. These experimental data were then combined with estimates for physical properties to compute experimental mass transfer coefficients which were corrected for axial mixing. Since these calculations were repetitious, a computer program was developed and used. In this appendix the calculational procedure and computer programs are described; then the results for all 37 runs conducted in the spray column are listed.

Estimates of Physical Properties.

The aqueous phase density and viscosity at the column temperature were taken as those listed by Weast (1970) for pure water. The solvent-phase density and viscosity were determined from data listed for pure solvents (API, 1963). The interfacial tension was estimated by the method of Donahue and Bartell (1952) as discussed in Section VII. The diffusivities for each solute in water and in the solvent were estimated by the method of Scheibel (1954) assuming that the values at infinite dilution would apply.

Computer Programs.

The majority of the spray column data reduction was done in the Fortran program SPRAY using a CDC 6400 computer. The experimental data, which were corrected for mass transfer during drop formation and coalescence in SPRAY, were then reduced in terms of the dispersion model using the Fortran program EVAL. The nomenclature used in this appendix while describing these programs is the same as that used in the computer programs; a listing of these programs follows this section.

Program SPRAY begins by solving the hydrodynamic equations. The superficial velocities of each phase, VD and VC, the column temperature, TEMP, and the physical property data are read in. From the total cross-sectional area of distributor plate holes, a discharge velocity, VZERO, is calculated and read in along with the hole diameter, DZERO. This information is used in a trial and error calculation to determine the drop diameter, DP. The method of Scheele and Meister (1968) is used to calculate DP since the discharge velocity in these experiments was always less than the jetting velocity.

The correlation of Minard and Johnson (1952) is used to calculate the continuous-phase flooding velocity, VCF, and the fraction of flooding, FF. The single drop terminal velocity, VT, is determined using the equations of Klee and Treybal (1956), and the method of Hughmark (1967) is used to calculate the hold-up, PHI, and the slip velocity, VS.

Program SPRAY continues by correcting the experimental data for end effects. The contact time for drop formation, CONTIME, and the interfacial area of the fully formed drop, AP, are calculated, which allows the mass transfer coefficient during drop formation to be calculated using equation (B8). The uncorrected aqueous-phase concentrations, XIN and XOUT (measured directly), and the solvent-phase concentrations, YIN (assumed to be zero) and YOUT (calculated by a material balance), are corrected for mass transfer during drop formation and drop coalescence. The corrected concentrations, CXIN, CXOUT, CYIN, and CYOUT, are the values used in the dispersion model to estimate mass transfer during drop rise. The continuous-phase Peclet number, PEC, based on the column height, COLHT, is calculated using equation (B6).

The calculations in program SPRAY are completed by determining theoretical estimates for the dispersed-phase number of transfer units, ND (equivalent to calculating the dispersed-phase mass transfer coefficient, k_d), and for the continuous-phase number of transfer units, NC. The interfacial area per unit of extractor volume, A, and the droplet rise (or fall) time, RT, are calculated. Theoretical estimates are made for oscillating drops using the theory of Angelo, et al. (1966; 1968) to calculate NDOD and NCOD, and for circulating drops using the equations of Ruby and Elgin (1955) to calculate NCRE, the equations of Hughmark (1967) to calculate NCHK, and the equation of Kronig and Brink (1950) to calculate NDKB.

The final step in determining the experimental values for the overall water-phase number of transfer units was accomplished using the program EVAL and subroutines FINDN and EETA. The subroutine EETA was described in Appendix C; it is used to solve the equations of the dispersion model. The continuous-phase Peclet number, PEC, is read into EVAL; a negative value of the dispersed-phase Peclet number, PED, is read in to signal that the dispersed phase travels through the extractor in plug flow (PED = ∞). A value of E, the extraction factor, and ZETA [η in equation (1), calculated from corrected concentrations] is read into EVAL for each component. By using the search subroutine FINDN, equation (3) is solved implicitly to determine NOW.

A listing of the programs follows. At the end of each program and subroutine listing, a typical output is shown for Run SS12A.

PROGRAM SPRAY

```
      PROGRAM SPRAY(INPUT.OUTPUT)
C* SPRAY ACCEPTS DATA FROM AN EXPERIMENTAL RUN AND CALCULATES DROP
C*** DIAMETER. HOLD-UP. PECLET NUMBER. AND MASS TRANSFER COEFFICIENTS.
C***
      DIMENSION NAME(6).DIFFD(6).DIFFC(6).E(6)
      REAL KD(6).KODF.KAPPA.NCOD.NDOD.NOW.NCHK.NCRE.NDKB
C************************** BEGIN FORMAT STATEMENTS ***********************
    1 FORMAT(A5.3X.A7.3X.A7.I5.2F10.3.F10.1.I5)
    2 FORMAT(1H1.20X.33HANALYSIS  OF  SPRAY  COLUMN  RUN .A5.10X.
     16HPAGE 1///17X.19HDISPERSED PHASE IS .A7.//17X.20HCONTINUOUS PHASE
     2 IS .A7.///14X.43H**** SUPERFICIAL VELOCITIES AND TEMPERATURE/23X.
     327HVELOCITY DISPERSED PHASE = .F6.2.6H FT/HR/23X.29HVELOCITY CONTI
     4NUOUS PHASE = .F6.2.6H FT/HR/23X.14HTEMPERATURE = .F4.1.
     5 10H DEGREES C//)
    3 FORMAT(2F10.5.F10.3.2F10.4)
    4 FORMAT(14X.24H**** PHYSICAL PROPERTIES/23X.26HDENSITY DISPERSED PH
     1ASE = .F7.5.8H GRAM/CC/23X.27HDENSITY CONTINUOUS PHASE = .F7.5.
     28H GRAM/CC/23X.22HINTERFACIAL TENSION = .F7.3.8H DYNE/CM/23X.
     328HVISCOSITY DISPERSED PHASE = .F7.4.3H CP/23X.
     429HVISCOSITY CONTINUOUS PHASE = .F7.4.3H CP//)
    5 FORMAT(F10.6.F10.5)
    6 FORMAT(14X.29H**** DISTRIBUTOR PLATE SIZING/23X..16HHOLE DIAMETER
     1= .F7.6.5H INCH/23X.21HDISCHARGE VELOCITY = .F7.5.7H FT/SEC/23X.
     2  22HSINGLE ORIFICE FLOW = .1PE9.3.8H CUFT/HR/23X.16HDROP DIAMETER
     3 = .0PF7.6.5H INCH//)
    7 FORMAT(14X.29H**** FLOODING CHARACTERISTICS/23X.31HCONT-PHASE FLOO
     1DING VELOCITY = .F6.2.6H FT/HR/23X.23HFRACTION OF FLOODING = .F6.
     22//)
    8 FORMAT(14X.34H**** HOLD-UP ESTIMATING PARAMETERS/23X.10HP**0.15 =
     1.F7.3/23X.21HOSCILLATION FACTOR = .F7.3/23X.27HTRANSITION DROP DIA
     2METER = .F7.6.5H INCH/23X.20HTERMINAL VELOCITY = .F7.2.
     3 6H FT/HR/23X.8HDPBAR = .F8.7.5H INCH/23X.11HDP/DPBAR = .F7.3/23X.
     4 7HVBAR = .F7.2.6H FT/HR//)
    9 FORMAT(14X.36H**** SOLUTION TO HOLD-UP CALCULATION/23X.10HHOLD-UP
     1= .F7.5/23X.16HSLIP VELOCITY = .F7.2.6H FT/HR//)
   10 FORMAT(1H1.20X.33HANALYSIS  OF  SPRAY  COLUMN  RUN .A5.10X.
     16HPAGE 2////)
   11 FORMAT(A8.2X.3F10.2)
   12 FORMAT(14X.62H**** SOLUTE DIFFUSIVITIES. DISTRIBUTION COEFFICIENTS
     1. AND E(I)/28X.15H10**5 * SQFT/HR/17X.6HSOLUTE.5X.5HDD(I).5X.
     2  5HDC(I).11X.5HKD(I).9X.4HE(I)/)
   13 FORMAT(16X.A8.F9.2.F10.2.F16.2.F13.2)
   14 FORMAT(1H0/14X.49H**** END EFFECT CORRECTION WITH SOLVENT DISPERSE
     1D/23X.16HFS/FW = FD/FC = .F6.3.6H LB/LB/23X.16HDROP DIAMETER = .
     2 F7.5.5H INCH/23X.15HORIFICE FLOW = .1PE9.3.8H CUFT/HR/23X
     3.15HCONTACT TIME = .F9.3.8H HR/DROP/23X.15HSURFACE AREA = .F9.2.
     410H SQFT/DROP//15X.6HSOLUTE.9X.4HFEED.5X.4HPROD.5X.4HFEED.5X.
     5 4HPROD.4X.7HOVERALL/23X.11H(PPM) WATER.4X.5HWATER.3X.7HSOLVENT.
     6  2X.7HSOLVENT.5X.4HZETA/)
   15 FORMAT(10X.3F10.1)
   16 FORMAT(14X.A8.5H MEAS.F8.1.3F9.1.F10.5)
   17 FORMAT(23X.4HCORR.F8.1.3F9.1.F10.5)
   18 FORMAT(1H0/14X.47H**** END EFFECT CORRECTION WITH WATER DISPERSED
     1/23X,16HFS/FW = FC/FD = ,F6.3,6H LB/LB/23X,16HDROP DIAMETER = ,
     2 F7.5,3H INCH/23X,15HORIFICE FLOW = ,1PE9.3,8H CUFT/HR/23X
     3,15HCONTACT TIME = ,E9.3,8H HR/DROP/23X,15HSURFACE AREA = ,E9.3,
     410H SQFT/DROP//15X,6HSOLUTE,9X,4HFEED,5X,4HPROD,5X,4HFEED,5X,
     5 4HPROD,4X,7HOVERALL/23X,11H(PPM) WATER,4X,5HWATER,3X,7HSOLVENT,
     6  2X,7HSOLVENT,5X,4HZETA/)
   19 FORMAT(F10.3)
   20 FORMAT(1H0/14X,29H**** AXIAL MIXING PARAMETERS/23X,12HLOCAL PEC =
     1,F7.4/23X,16HCOLUMN HEIGHT = ,F6.3,3H FT/23X,14HOVERALL PEC = ,
     2  F7.4//)
   21 FORMAT(1H1,20X,33HANALYSIS  OF  SPRAY  COLUMN  RUN ,A5,10X,
     1 6HPAGE 3////14X,28H**** MASS TRANSFER ESTIMATES/23X,4HA = ,F6.2,
     2 10H SQFT/CUFT/23X,12HRISE TIME = ,1PE10.3,3H HR//)
   22 FORMAT(1H1,20X,33HANALYSIS  OF  SPRAY  COLUMN  RUN ,A5,10X,
     1 6HPAGE 3////14X,28H**** MASS TRANSFER ESTIMATES/23X,4HA = ,F6.2,
     2 10H SQFT/CUFT/23X,12HFALL TIME = ,1PE10.3,3H HR//)
   23 FORMAT(14X,47H**** OSCILLATING DROPS (SURFACE STRETCH THEORY)/
     1 23X,4HB = ,F6.4,/23X,4HW = ,1PE9.3,4H /HR//15X,6HSOLUTE,6X,2HNC,
     2  7X,2HND,8X,1HR,7X,3HNOW,4X,5H1/NOW,4X,3H1/E/)
   24 FORMAT(14X,A8,4F9.4,F8.4,F9.4)
   25 FORMAT(1H0/14X,38H**** CIRCULATING DROPS - HK = HUGHMARK/39X,
     1  15HRE = RUBY-ELGIN/39X,17HKB = KRONIG-BRINK/22X,18HHK FACTORS -
     2RE = ,F6.1/35X,8HKAPPA = ,F7.4/35X,4HF = ,F6.3//15X,6HSOLUTE,5X,
     3  5HNC,HK,4X,5HNC,RE,4X,5HND,KB,6X,1HR,7X,3HNOW,4X,5H1/NOW/)
   26 FORMAT(14X,A8,5F9.4,F8.4)
C*********************** END OF FORMAT STATEMENTS *********************
C***
C*** READ IN AND PRINT EXPERIMENTAL CONDITIONS
   31 READ 1,RUNNUM,NAMED,NAMEC,IDISP,VD,VC,TEMP,NCOMPS
      IF(IDISP.EQ.0) GO TO 100
C*** IF IDISP=1, SOLVENT IS DISPERSED. IF IDISP=2, WATER IS DISPERSED.
      PRINT 2,RUNNUM,NAMED,NAMEC,VD,VC,TEMP
C*** READ AND PRINT PHYSICAL PROPERTY DATA (GM/CC,GM/CC,DYNE/CM,CP,CP)
      READ 3,DENSD,DENSC,SIGMA,VISCD,VISCC
      DELDEN = ABS(DENSD - DENSC)
      PRINT 4,DENSD,DENSC,SIGMA,VISCD,VISCC
C*** READ IN DISTRIBUTOR PLATE HOLE DIAMETER AND DISCHARGE VELOCITY
C***                             (INCH)                  (FT/SEC)
C*** TO BYPASS DISTRIBUTOR CALCULATION, READ DZERO = DP AND VZERO = 0.0
      READ 5,DZERO,VZERO
      SOFLOW = 78.54*VZERO*DZERO*DZERO
      IF(VZERO .NE. 0.0) GO TO 32
      DP = DZERO
      DZERO = 0.0
      GO TO 40
C*** CALCULATE DROPLET DIAMETER
   32 A = 2.877E-07*SIGMA*DZERO/DELDEN - 1.694E-04*DENSD*
     1  (DZERO*VZERO)**2/DELDEN + 8.403E-05*DZERO**2*((VZERO/DELDEN)**2*
     2  DENSD*SIGMA)**0.33333
      B = 4.380E-05*VISCC*VZERO*DZERO**3/DELDEN
      DP = 2.0*DZERO
      DO 39 I=1,3
      Y = A + B/DP/DP
      X = DZERO/12.0/Y**0.33333
      IF(X.GT. 0.5) GO TO 35
      F = 1.0000 - 0.7506*X + 0.4572*X*X
      GO TO 39
   35 IF(X,GT. 1.7) GO TO 37
      F = 0.9246 - 0.4490*X + 0.1556*X*X
      GO TO 39
   37 F = 0.4198 + 0.1125*X
   39 DP = 14.89*(F*Y)**0.33333
   40 PRINT 6,DZERO,VZERO,SOFLOW,DP
C*** CALCULATE FLOODING VELOCITY OF CONTINUOUS PHASE
      VCF = 3.132E+04*DELDEN**0.28/(4.077*VISCC**0.075*SQRT(DENSC)
     1  + 6.873*DP**0.056*SQRT(DENSD*VD/VC++M-2
      FF = VC/VCF
      PRINT 7,VCF,FF
C*** CALCULATE HOLD-UP ESTIMATING PARAMETERS
      P = (1.029E+05*DENSC*DENSC*SIGMA**3/VISCC**4/DELDEN)**0.15
      OSCFACT = 8419.*DELDEN*DP*DP*P/SIGMA
      DPT = 9.127E-02*SQRT(SIGMA/DELDEN/P)
      IF(DP.GT.DPT) GO TO 44
      VT = 1.443E+04*EXP(0.58*ALOG(DELDEN) + 0.70*ALOG(DP) - 0.45*ALOG(
     1    DENSC) - 0.11*ALOG(VISCC))
      GO TO 45
   44 VT = 1.310E+03*EXP(0.28*ALOG(DELDEN) + 0.10*ALOG(VISCC)
     1    + 0.18*ALOG(SIGMA) - 0.55*ALOG(DENSC))
   45 DPBAR = 1.670E-03*(VISCC*VISCC/DENSC/DELDEN)**0.33333
      A = DP/DPBAR
      VBAR = 278.6*(VISCC*DELDEN/DENSC/DENSC)**0.33333
      PRINT 8,P,OSCFACT,DPT,VT,DPBAR,A,VBAR
C*** CALCULATE HOLD-UP AND SLIP VELOCITY
      X = VD/VT
      IF(X,GT. 0.02) GO TO 46
      H = X
      GO TO 50
   46 IF(X,GT. 0.05) GO TO 48
      H = -0.0023 + 1.11*X
      GO TO 50
   48 H = -0.0285 + 1.36*X + 2.98*X*X
   50 X = VD/H
      Y = X + VD - VC
      PHI = (Y - SQRT(Y*Y - 4.0*VD*X))/2.0/X
      VS = VD/PHI + VC/(1.0 - PHI)
      PRINT 9,PHI,VS
      PRINT 10,RUNNUM
C*** READ IN AND PRINT DIFFUSIVITIES
      DO 54 I=1,NCOMPS
C***           (-,10**5*SQFT/HR,10**5*SQFT/HR,-)
   54 READ 11,NAME(I),DIFFD(I),DIFFC(I),KD(I)
      FDOFC = FSOFW = DENSD*VD/DENSC/VC
      IF(IDISP.EQ.2) FSOFW = 1.0/FDOFC
C*** PRINT DIFFUSIVITIES, DISTRIBUTION COEFFICIENTS, AND E(I)
      PRINT 12
      DO 55 I=1,NCOMPS
      E(I) = FSOFW*KD(I)
   55 PRINT 13,NAME(I),DIFFD(I),DIFFC(I),KD(I),E(I)
C*** CALCULATE END EFFECT CORRECTION
      CONTIME = 3.030E-04*DP*DP*DP/SOFLOW
      AP = 2.182E-02*DP*DP
      IF(IDISP.EQ.2) GO TO 70
      PRINT 14,FSOFW,DP,SOFLOW,CONTIME,AP
      DO 60 I=1,NCOMPS
      READ 15,XIN,XOUT,YIN
      YOUT = YIN + (XIN - XOUT)/FSOFW
      ZETA = (XOUT - YIN/KD(I))/(XIN - YIN/KD(I))
      PRINT 16,NAME(I),XIN,XOUT,YIN,YOUT,ZETA
      DYBOT = XOUT*KD(I) - YIN
      DYTOP = XIN*KD(I) - YOUT
      DY = 9.125*AP*SQRT(DIFFD(I)*CONTIME)*DYBOT/DP**3/(1.0 +
     1  DENSD*SQRT(DIFFD(I)/DIFFC(I))*KD(I)/DENSC)
      CYIN = YIN + DY
      CXOUT = XOUT + DY*FSOFW
      DY = DY*DYTOP/DYBOT
      CYOUT = YOUT - DY
      CXIN = XIN - DY*FSOFW
      ZETA = (CXOUT - CYIN/KD(I))/(CXIN - CYIN/KD(I))
   60 PRINT 17,CXIN,CXOUT,CYIN,CYOUT,ZETA
      GO TO 80
   70 PRINT 18,FSOFW,DP,SOFLOW,CONTIME,AP
      DO 71  I=1,NCOMPS
      READ 15,XIN,XOUT,YIN
      YOUT = YIN + (XIN - XOUT)/FSOFW
      ZETA = (XOUT - YIN/KD(I))/(XIN - YIN/KD(I))
      PRINT 16,NAME(I),XIN,XOUT,YIN,YOUT,ZETA
      DXTOP = XIN - YOUT/KD(I)
      DXBOT = XOUT - YIN/KD(I)
      DX = 9.125*AP*SQRT(DIFFD(I)*CONTIME)*DXTOP/DP**3/(1.0 +
     1  DENSD*SQRT(DIFFD(I)/DIFFC(I))/KD(I)/DENSC)
      CXIN = XIN - DX
      CYOUT = YOUT - DX/FSOFW
      DX = DX*DXBOT/DXTOP
      CXOUT = XOUT + DX
      CYIN = YIN + DX/FSOFW
      ZETA = (CXOUT - CYIN/KD(I))/(CXIN - CYIN/KD(I))
   71 PRINT 17,CXIN,CXOUT,CYIN,CYOUT,ZETA
C*** CALCULATE CONTINUOUS-PHASE PECLET NUMBER
   80 READ 19,COLHT
      PECL = 2.36*PHI**0.33333
      EC = VS*DP/PECL/12.0
      PEC = VC*COLHT/EC/(1.0 - PHI)
      PRINT 20,PECL,COLHT,PEC
C*** CALCULATE MASS TRANSFER ESTIMATES
      A = 72.0*PHI/DP
      RT = COLHT*PHI/VD
      IF(IDISP.EQ.2) GO TO 81
      PRINT 21,RUNNUM,A,RT
      GO TO 82
   81 PRINT 22,RUNNUM,A,RT
C*** FIRST FOR OSCILLATING DROPS - SURFACE STRETCH THEORY
   82 B = 0.4602*DP**0.225
      W = 1966.*SQRT(SIGMA*9/DP**3/(3.*DENSD + 2.*DENSC))
      PRINT 23,B,W
      B = A*COLHT/VD
      DO 85  I=1,NCOMPS
      NDOD = 1.244*SQRT(1.0E-05*DIFFD(I)*W)*B
      NCOD = NDOD*SQRT(DIFFC(I)/DIFFD(I))*VD/VC
      IF(IDISP.EQ.2) GO TO 84
      C = 1.0/NCOD + 1.0/F(I)/NDOD
      NOW = 1.0/C
      R = NCOD/E(I)/NDOD
      D = 1.0/E(I)
      GO TO 85
   84 C = 1.0/NDOD + 1.0/E(I)/NCOD
      NOW = 1.0/C
      R = NDOD/E(I)/NCOD
      D = 1.0/E(I)
   85 PRINT 24.NAME(I).NCOD.NDOD.R.NOW.C.D
C*** NOW FOR CIRCULATING DROPS
      RE = 2.150*DP*VS*DENSC/VISCC
      KAPPA = EXP(ALOG(RE)/8.0 + ALOG(VISCC/VISCD)/4.0 + ALOG(8.432E-05*
     1VS*VISCC/SIGMA)/6.0)
      F = 0.281 + 1.615*KAPPA + 3.73*KAPPA*KAPPA - 1.844*KAPPA**3
      BHK = 0.463*RE**0.484
      BRE = 0.725*(1.0 - PHI)*RE**0.57
      B = 1.2E-04*A*COLHT/DP/VC
      PRINT 25.RE.KAPPA.F
      DO 88 I=1.NCOMPS
      D = 1.342E+05*DP/DIFFC(I)**0.66667
      SC = 3875.*VISCC/DENSC/DIFFC(I)
      NCHK = (2.0 + BHK*SC**0.339*D**0.072)*F*B*DIFFC(I)
      NCRE = BRE*SC**0.42*B*DIFFC(I)
      XOLAM = 9.216E-02*DIFFD(I)*RT/DP/DP
      NDKB = -ALOG(0.6240*EXP(-1.656*XOLAM) + 0.1332*EXP(-9.08*XOLAM)
     1 + 0.05587*EXP(-22.2*XOLAM))
      IF(IDISP.EQ.2) GO TO 87
      C = 1.0/NCRE + 1.0/E(I)/NDKB
      NOW = 1.0/C
      R = NCRE/E(I)/NDKB
      GO TO 88
   87 C = 1.0/NDKB + 1.0/E(I)/NCRE
      NOW = 1.0/C
      R = NDKB/E(I)/NCRE
   88 PRINT 26.NAME(I).NCHK.NCRE.NDKB.R.NOW.C
      GO TO 31
  100 CONTINUE
      END SPRAY
     ANALYSIS  OF  SPRAY  COLUMN  RUN SS12A            PAGE

   DISPERSED PHASE IS IBUTENE

   CONTINUOUS PHASE IS WATER

**** SUPERFICIAL VELOCITIES AND TEMPERATURE
        VELOCITY DISPERSED PHASE =  52.25 FT/HR
        VELOCITY CONTINUOUS PHASE =  23.26 FT/HR
        TEMPERATURE = 21.6 DEGREES C

**** PHYSICAL PROPERTIES
        DENSITY DISPERSED PHASE =  .59140 GRAM/CC
        DENSITY CONTINUOUS PHASE =  .99790 GRAM/CC
        INTERFACIAL TENSION =  41.500 DYNE/CM
        VISCOSITY DISPERSED PHASE =   .1820 CP
        VISCOSITY CONTINUOUS PHASE =   .9704 CP

**** DISTRIBUTOR PLATE SIZING
        HOLE DIAMETER = .062500 INCH
        DISCHARGE VELOCITY =  .12360 FT/SEC
        SINGLE ORIFICE FLOW = 3.792E-02 CUFT/HR
        DROP DIAMETER = .181074 INCH

**** FLOODING CHARACTERISTICS
        CONT-PHASE FLOODING VELOCITY = 194.91 FT/HR
        FRACTION OF FLOODING = .11934

**** HOLD-UP ESTIMATING PARAMETERS
        P**0.15 =  35.171
        OSCILLATION FACTOR =  95.939
        TRANSITION DROP DIAMETER = .155500 INCH
        TERMINAL VELOCITY = 1997.26 FT/HR
        DPBAR = .0022112 INCH
        DP/DPBAR =  82.250
        VBAR =  204.61 FT/HR

**** SOLUTION TO HOLD-UP CALCULATION
        HOLD-UP =  .02722
        SLIP VELOCITY = 1943.48 FT/HR
        ANALYSIS  OF  SPRAY  COLUMN  RUN SS12A          PAGE 2


**** SOLUTE DIFFUSIVITIES, DISTRIBUTION COEFFICIENTS, AND E(I)
               10**5 * SQFT/HR
  SOLUTE       DD(I)     DC(I)               KD(I)          E(I)

 ACETONE       26.20      4.22                 .63           .84
 MEK           24.00      3.87                2.49          3.31
 CROTONAL      24.00      3.88                2.48          3.30
 N-BU ACE      20.40      2.71              168.00        223.66

**** END EFFECT CORRECTION WITH SOLVENT DISPERSED
        FS/FW = FD/FC =  1.331 LB/LB
        DROP DIAMETER =  .18187 INCH
        ORIFICE FLOW = 3.792E-02 CUFT/HR
        CONTACT TIME = 4.897E-05 HR/DROP
        SURFACE AREA = 7.218E-04 SQFT/DROP

 SOLUTE          FEED      PROD      FEED      PROD     OVERALL
          (PPM) WATER     WATER    SOLVENT   SOLVENT     ZETA

ACETONE  MEAS  2058.0    1307.0       0.      564.1     .63508
         CORR  2038.4    1329.1     16.6      549.4     .64747
MEK      MEAS  4167.0    1579.0       0.     1944.0     .37893
         CORR  4077.7    1620.6     31.3     1876.9     .39558
CROTONAL MEAS  4422.0    1620.0       0.     2104.7     .36635
         CORR  4327.8    1662.7     32.1     2034.0     .38235
N-BU ACE MEAS  2212.0     620.0       0.     1195.8     .28029
         CORR  2153.3     637.3     13.0     1149.5     .29636

**** AXIAL MIXING PARAMETERS
        LOCAL PEC =    .7099
        COLUMN HEIGHT =  3.500 FT
        OVERALL PEC =  2.0170
        ANALYSIS  OF  SPRAY  COLUMN  RUN SS12A          PAGE 3


**** MASS TRANSFER ESTIMATES
        A =  10.78 SQFT/CUFT
        RISE TIME =  1.923E-03 HR


**** OSCILLATING DROPS (SURFACE STRETCH THEORY)
        B =  .3136
        W = 4.710E+04 /HR

 SOLUTE        NC         ND          R          NOW     1/NOW      1/E

ACETONE     2.8436     3.1542     1.0749     1.3705     .7297     1.1923
MEK         2.7231     3.0188      .2721     2.1406     .4672      .3017
CROTONAL    2.7266     3.0188      .2736     2.1409     .4671      .3029
N-BU ACE    2.2787     2.7832      .0037     2.2704     .4404      .0045


**** CIRCULATING DROPS - HK = HUGHMARK
                         RE = RUBY-ELGIN
                         KB = KRONIG-BRINK
       HK FACTORS - RE =  761.5
                    KAPPA =  1.3822
                    F =  4.770

 SOLUTE       NC,HK      NC,RE      ND,KB        R          NOW     1/NOW

ACETONE     4.6665     2.4623      .6102     4.8114      .4237   2.3602
MEK         4.6325     2.3417      .5840     1.2057     1.0598     .9436
CROTONAL    4.6379     2.3452      .5840     1.2164     1.0581     .9451
N-BU ACE    3.7195     1.9045      .5393      .0158     1.8749     .5334
```

PROGRAM EVAL

```
      PROGRAM EVAL(INPUT.OUTPUT)
C* EVAL ACCEPTS EXPERIMENTAL DATA FROM EXTRACTING SOLUTES FROM WATER
C*** AND ANALYZES THEM IN TERMS OF THE DISPERSION MODEL
      DIMENSION NAME(6).E(6).ZETA(6).Z(9).U(101).V(101)
      REAL NOX.NOA
      DATA AMI/5HINFIN/.UNO/7HUNDETER/
C*** BEGIN FORMAT STATEMENTS *******************************************
    1 FORMAT(I5)
    2 FORMAT(2F10.4.A5.I5)
    3 FORMAT(A8.2X.F10.4.F10.5)
   11 FORMAT(1H1.15X.43HANALYSIS OF DATA FOR EXTRACTION RUN NUMBER .A5//
     110X.6HPEX = .F8.4.5X,6HPEY = .F8.4.I24.11H COMPONENTS/)
   12 FORMAT(1H1.15X.43HANALYSIS OF DATA FOR EXTRACTION RUN NUMBER .A5//
     110X.6HPEX = .F8.4.5X,7HPEY =  .A5.I24.11H COMPONENTS/)
   13 FORMAT(10H0**** FOR ,A8.6H  E = .F8.4.12H AND ZETA = .F6.5.14H GIV
     1ING NOX = .F7.3//        80H *PROFILE Z(0.0)  Z(0.1)  Z(0.2)  Z(0.3
     2)  Z(0.5)  Z(0.7)  Z(0.8)  Z(0.9)  Z(1.0)/2X.6HMIXED .9F8.5)
   14 FORMAT(10H0**** FOR ,A8.6H  E = .F8.4.12H AND ZETA = .F6.5.14H GIV
     1ING NOX = .A7//)
   15 FORMAT(6X.40HNO SOLUTION POSSIBLE FOR NOX .LT. 100.00/)
   16 FORMAT(6X.39HTRIAL AND ERROR SEARCH DID NOT CONVERGE/)
   17 FORMAT(2X.6HPLUG   .9F8.5/)
   18 FORMAT(71H *SENSITIVITY -- DX = CHANGE IN NOX CAUSED BY A 1 PERCEN
     1T DECREASE IN X/5X.8HDZETA = .1PE9.2.8H . DE = .E9.2.10H . DPEX =
     2.E9.2.10H . DPEY = .E9.2/)
C*** END OF FORMAT STATEMENTS *******************************************
C*** READ IN NUMBER OF RUNS
      READ 1.NRUNS
      DO 30 NR=1.NRUNS
C*** READ IN PEX. PEY. RUN NUMBER. AND NUMBER OF COMPONENTS
      READ 2.PEX.PEY.RNUM.NCOMPS
C*** READ IN E AND ZETA FOR EACH COMPONENT
      DO 20 I=1.NCOMPS
   20 READ 3.NAME(I).E(I).ZETA(I)
      IF(PEY.LT.0.0) GO TO 21
C*** PRINT HEADINGS
      PRINT 11.RNUM.PEX.PEY.NCOMPS
      GO TO 22
   21 PRINT 12.RNUM.PEX.AMI.NCOMPS
   22 DO 30 NC=1.NCOMPS
C*** SOLVE FOR NOX FOR EACH COMPONENT
      EA = E(NC)
      ZA = ZETA(NC)
      CALL FINDN(PEX.PEY.EA.ZA.NOX.Z)
      IF(NOX.GT. 100.00) GO TO 29
      PRINT 13.NAME(NC).E(NC).ZETA(NC).NOX.(Z(J).J=1.9)
C*** CALCULATE PROFILE FOR PLUG FLOW
      IF(E(NC).EQ. 1.0) GO TO 25
      FA = 1.0 - 1.0/E(NC)
      NOA = ALOG(EA/ZETA(NC) + 1.0/E(NC))/FA
      EA = -FA*NOA
      ZA = -EXP(EA)/E(NC)
      J = 0
      DO 23 I=1,11
      IF(I.EQ.5 .OR. I.EQ.7) GO TO 23
      J = J + 1
      X = FLOAT(I - 1)/10.0
      Z(J) = (ZA + EXP(EA*X))/(1.0 + ZA)
   23 CONTINUE
      GO TO 27
   25 NOA = 1.0/ZETA(NC) - 1.0
      EA = NOA + 1.0
      J = 0
      DO 26 I=1,11
      IF(I.EQ.5 .OR. I.EQ.7) GO TO 26
      J = J + 1
      X = FLOAT(I - 1)/10.0
      Z(J) = (1.0 + NOA*(1.0 - X))/EA
   26 CONTINUE
   27 PRINT 17,(Z(J),J=1,9)
C*** CALCULATE SENSITIVITY
      NOA = 1.01*NOX
      EA = E(NC)
      CALL EETA(PEX,PEY,EA,NOA,ZE,1,Z,U,V)
      DN = (ZE - ZETA(NC))/(0.01*NOX)
      DNDZ = -0.01*ZETA(NC)/DN
      EA = 0.99*E(NC)
      CALL EETA(PEX,PEY,EA,NOX,ZE,1,Z,U,V)
      DNDE = (ZETA(NC) - ZE)/DN
      PEA = 0.99*PEX
      EA = E(NC)
      CALL EETA(PEA,PEY,EA,NOX,ZE,1,Z,U,V)
      DNDPX = (ZETA(NC) - ZE)/DN
      DPY = 0.0
      DNDPY = 0.0
      IF(PEY.LT.0.0) GO TO 28
      PEA = 0.99*PEY
      CALL EETA(PEX,PEA,EA,NOX,ZE,1,Z,U,V)
      DNDPY = (ZETA(NC) - ZE)/DN
   28 PRINT 18,DNDZ,DNDE,DNDPX,DNDPY
      GO TO 30
C*** PRINT OUT RESULTS
   29 PRINT 14,NAME(NC),E(NC),ZETA(NC),UND
      IF(NOX.EQ. 100.01) PRINT 15
      IF(NOX.EQ. 100.02) PRINT 16
   30 CONTINUE
      END EVAL
```

SUBROUTINE FINDN

```
      SUBROUTINE FINDN(PEX,PEY.E.ZETA.NOX.Z)
C* FINDN DETERMINES NOX WHEN PEX. PEY. E. AND ZETA ARE GIVEN.  IF PEY IS
C*** .LT. 0.0 . THE SOLUTION IS FOR NO BACKMIXING IN THE ORGANIC PHASE.
C*** IF E IS LESS THAN 0.0 . THEN CALCULATION IS FOR INFINITE E.
C*** IF NO SOLUTION EXISTS FOR WHICH NOX .LT. 100. . THE PROGRAM RETURNS
C*** WITH NOX = 100.01  IF THE PROGRAM DOES NOT CONVERGE. NOX = 100.02
      DIMENSION Z(9).U(101).V(101)
      REAL NOX.NA.NB
C*** FIRST DETERMINE THE MINIMUM ZETAM WITH INFINITE MASS TRANSFER
      IF(E.LT. 0.0) GO TO 10
      IF(PEY.GE. 0.0) GO TO 3
      IF(E.EQ. 1.0) GO TO 2
      DUM = EXP(E*PEX*(1.0/E - 1.0))
    1 ZETAM = (E*DUM - DUM)/(E*E - DUM)
      GO TO 5
    2 ZETAM = 1.0/(2.0 + PEX)
      GO TO 5
    3 IF(E.EQ. 1.0) GO TO 4
      DUM = EXP(PEX*PEY*(1.0/E - 1.0)/(PEX + PEY/E))
      GO TO 1
    4 ZETAM = (PEX + PEY) / (2.0*(PEX + PEY) + PEX*PEY)
    5 IF(ZETA.GT.ZETAM) GO TO 10
    6 NOX = 100.01
      GO TO 60
C*** NOW BEGIN TRIAL AND ERROR SEARCH FOR NOX
   10 NA = 4.00
      DO 16 ITER =1.20
      CALL EETA(PEX.PEY.E.NA.ZETACAL.1.Z.U.V)
      IF(ABS(ZETACAL - ZETA).LT. 0.00001) GO TO 16
      NB = NA + 0.1
      CALL EETA(PEX.PEY.E.NB.ZETAB.1.Z.U.V)
      DFDN = 10.0*ALOG(ZETAB/ZETACAL)
      NOX = NA - ALOG(ZETACAL/ZETA)/DFDN
      IF(NOX.GT. 100.0) GO TO 14
      IF(NOX.GT.0.0) GO TO 15
      NOX = 0.5*NA
      GO TO 15
   14 IF(NA.EQ. 99.00) GO TO 6
      NOX = 99.00
   15 NA = NOX
      NOX = 100.02
      RETURN
   16 NOX = NA
      CALL EETA(PEX.PEY.E.NOX.ZETAB.2.Z.U.V)
   60 RETURN
      END FINDN
```

```
                 ANALYSIS OF DATA FOR EXTRACTION RUN NUMBER SS12A

        PEX =   2.0170      PEY =  INFIN                              4 COMPONENTS

**** FOR ACETONE    E =     .8400 AND ZETA = .64747 GIVING NOX =     .694

*PROFILE Z(0.0)  Z(0.1)  Z(0.2)  Z(0.3)  Z(0.5)  Z(0.7)  Z(0.8)  Z(0.9)  Z(1.0)
 MIXED    .85094  .82627  .80009  .77265  .72143  .67871  .66259  .65160  .64747
 PLUG    1.00000  .96646  .93255  .89826  .82056  .75731  .72110  .68449  .64747

*SENSITIVITY -- DX = CHANGE IN NOX CAUSED BY A 1 PERCENT DECREASE IN X
    DZETA =  2.55E-02 , DE =  3.30E-03 , DPEX =  7.65E-04 , DPEY =  0.


**** FOR MEK          E =   3.3100 AND ZETA = .39558 GIVING NOX =   1.403

*PROFILE Z(0.0)  Z(0.1)  Z(0.2)  Z(0.3)  Z(0.5)  Z(0.7)  Z(0.8)  Z(0.9)  Z(1.0)
 MIXED    .72387  .67020  .62655  .57491  .49613  .43617  .41464  .40075  .39557
 PLUG    1.00000  .91801  .84175  .77084  .64355  .53346  .48413  .43825  .39556

*SENSITIVITY -- DX = CHANGE IN NOX CAUSED BY A 1 PERCENT DECREASE IN X
    DZETA =  2.16E-02 , DE =  2.63E-03 , DPEX =  2.29E-03 , DPEY =  0.


**** FOR CROTONAL  E =   3.3000 AND ZETA = .38235 GIVING NOX =   1.478

*PROFILE Z(0.0)  Z(0.1)  Z(0.2)  Z(0.3)  Z(0.5)  Z(0.7)  Z(0.8)  Z(0.9)  Z(1.0)
 MIXED    .71709  .66215  .61141  .56484  .48480  .42373  .40195  .38761  .38235
 PLUG    1.00000  .91526  .83671  .76385  .63363  .52164  .47166  .42532  .38235

*SENSITIVITY -- DX = CHANGE IN NOX CAUSED BY A 1 PERCENT DECREASE IN X
    DZETA =  2.22E-02 , DE =  2.95E-03 , DPEX =  2.56E-03 , DPEY =  0.


**** FOR N-BU ACE  E = 223.0000 AND ZETA = .29636 GIVING NOX =   1.678

*PROFILE Z(0.0)  Z(0.1)  Z(0.2)  Z(0.3)  Z(0.5)  Z(0.7)  Z(0.8)  Z(0.9)  Z(1.0)
 MIXED    .66463  .58685  .52042  .47879  .39445  .33450  .31416  .30107  .29636
 PLUG    1.00000  .88561  .78429  .69455  .54464  .42703  .37810  .33475  .29636

*SENSITIVITY -- DX = CHANGE IN NOX CAUSED BY A 1 PERCENT DECREASE IN X
    DZETA =  1.80E-02 , DE =  5.04E-05 , DPEX =  2.79E-03 , DPEY =  0.
```

List of Experimental Data.

In the Table G to follow, the experimental data for all 37 runs conducted in the spray column extractor are listed. The table entries include the measured phase velocities (based on a 1 inch column diameter), the column temperature, and the feed and product aqueous-phase concentrations. F_s/F_w is the solvent mass flow rate divided by the water mass flow rate; when this quantity is multiplied by K_d, the extraction factor, E, for each solute results. Also included in the table are the estimates of physical properties and the following quantities calculated during the computer data reduction:

d_p = drop diameter
ϕ = dispersed phase hold-up
a = interfacial area per column volume
Pe_c = continuous-phase Peclet number
FF = percentage of flooding
RT = dispersed phase rise (or fall) time

Table G. Spray Column Data

Spray column run # SS1 Temperature = 22.7°C

Dispersed phase = Isobutylene

Continuous phase = Prepared waste water

V_d = 82.43 ft/hr, V_c = 19.38 ft/hr, F_s/F_w = 2.519

ρ_d = 0.5908 gm/cc, μ_d = 0.180 cp,

ρ_c = 0.9976 gm/cc, μ_c = 0.942 cp, σ = 41.5 dyne/cm

d_p = 0.1865 inch, ϕ = 0.0443, a = 17.11 ft^2/ft^3

Pe_c = 2.029, FF = 15.3%, RT = 6.78 seconds

Solute	D_d	D_c	K_d	Feed Water (ppm)	Product Water (ppm)	% Removal
	$(10^5 \cdot ft^2/hr)$					
1. Phenol	23.7	3.51	0.70	20000	4180	79.1
2. o-Cresol	22.0	3.08	4.80	10000	492	95.1

Table G. Spray Column Data (Continued)

Spray column run # SS2 Temperature = 21.2 °C

Dispersed phase = Isobutylene

Continuous phase = Prepared waste water

V_d = 71.63 ft/hr, V_c = 22.18 ft/hr, F_s/F_w = 1.918

ρ_d = 0.5927 gm/cc, μ_d = 0.182 cp,

ρ_c = 0.9980 gm/cc, μ_c = 0.975 cp, σ = 41.8 dyne/cm

d_p = 0.1857 inch, ϕ = 0.0381, a = 14.79 ft^2/ft^3

Pe_c = 2.179, FF = 14.5 %, RT = 6.71 seconds

Solute	D_d	D_c	K_d	Feed Water (ppm)	Product Water (ppm)	% Removal
	($10^5 \cdot ft^2/hr$)					
1. Phenol	23.3	3.39	0.70	16900	2001	88.2
2. o-Cresol	21.6	2.98	4.80	1300	44.0	96.6

Table G. Spray Column Data (Continued)

Spray column run # SS3 Temperature = 20.6 °C

Dispersed phase = Isobutylene

Continuous phase = Lube oil refining waste water

V_d = 71.63 ft/hr, V_c = 22.18 ft/hr, F_s/F_w = 1.920

ρ_d = 0.5934 gm/cc, μ_d = 0.183 cp,

ρ_c = 0.9981 gm/cc, μ_c = 0.991 cp, σ = 41.9 dyne/cm

d_p = 0.1859 inch, ϕ = 0.0381 , a = 14.74 ft^2/ft^3

Pe_c = 2.171, FF = 14.6 %, RT = 6.70 seconds

Solute	D_d	D_c	K_d	Feed Water (ppm)	Product Water (ppm)	% Removal
	($10^5 \cdot ft^2/hr$)					
1. Phenol	23.1	3.33	0.70	17000	10100	40.6
2. o-Cresol	21.5	2.93	4.80	1200	397	66.9

Comments: May have been phenol and o-cresol in the feed solvent (See Chapter V).

Spray column run # SS4A Temperature = 22.5 °C

Dispersed phase = Isobutylene

Continuous phase = Prepared waste water

V_d = 71.63 ft/hr, V_c = 22.52 ft/hr, F_s/F_w = 1.884

ρ_d = 0.5911 gm/cc, μ_d = 0.180 cp,

ρ_c = 0.9977 gm/cc, μ_c = 0.947 cp, σ = 41.5 dyne/cm

d_p = 0.1850 inch, ϕ = 0.0383, a = 14.90 ft^2/ft^3

Pe_c = 2.231, FF = 14.5%, RT = 6.73 seconds

Solute	D_d	D_c	K_d	Feed Water (ppm)	Product Water (ppm)	% Removal
	($10^5 \cdot ft^2/hr$)					
1. Phenol	23.7	3.51	0.70	17850	2570	85.6
2. o-Cresol	22.0	3.08	4.80	1450	59.0	96.1

Table G. Spray Column Data (Continued)

Spray column run # SS4B Temperature = 22.5 °C

Dispersed phase = Isobutylene

Continuous phase = Prepared waste water

V_d = 52.50 ft/hr, V_c = 22.52 ft/hr, F_s/F_w = 1.381

ρ_d = 0.5911 gm/cc, μ_d = 0.180 cp,

ρ_c = 0.9977 gm/cc, μ_c = 0.947 cp, σ = 41.5 dyne/cm

d_p = 0.1818 inch, ϕ = 0.0274, a = 10.86 ft^2/ft^3

Pe_c = 1.964, FF = 11.8%, RT = 6.58 seconds

Solute	D_d ($10^5 \cdot ft^2/hr$)	D_c ($10^5 \cdot ft^2/hr$)	K_d	Feed Water (ppm)	Product Water (ppm)	% Removal
1. Phenol	23.7	3.51	0.70	17850	4280	76.0
2. o-Cresol	22.0	3.08	4.80	1450	68.0	95.3

Spray column run # SS5 Temperature = 21.2 °C

Dispersed phase = Isobutylene

Continuous phase = Prepared waste water

V_d = 52.25 ft/hr, V_c = 23.31 ft/hr, F_s/F_w = 1.312

ρ_d = 0.5927 gm/cc, μ_d = 0.182 cp,

ρ_c = 0.9979 gm/cc, μ_c = 0.976 cp, σ = 41.8 dyne/cm

d_p = 0.1825 inch, ϕ = 0.0272, a = 10.73 ft^2/ft^3

Pe_c = 2.012, FF = 12.0%, RT = 6.56 seconds

Solute	D_d ($10^5 \cdot ft^2/hr$)	D_c ($10^5 \cdot ft^2/hr$)	K_d	Feed Water (ppm)	Product Water (ppm)	% Removal
1. Phenol	23.3	3.39	(0.7)	12900	2580	80.0
2. VinylAc	23.5	3.45	52.0	12000	97.0	99.2

Comments: The presence of vinyl acetate in the solvent phase probably increased K_d for phenol.

Table G. Spray Column Data (Continued)

Spray column run # SS6A Temperature = 21.7°C

Dispersed phase = Isobutylene

Continuous phase = Lube oil refining waste water

V_d = 92.24 ft/hr, V_c = 21.56 ft/hr, F_s/F_w = 2.535

ρ_d = 0.5913 gm/cc, μ_d = 0.182 cp,

ρ_c = 0.9978 gm/cc, μ_c = 0.965 cp, σ = 41.5 dyne/cm

d_p = 0.1882 inch, ϕ = 0.0499, a = 19.07 ft^2/ft^3

Pe_c = 2.348, FF = 17.1%, RT = 6.81 seconds

Solute	D_d	D_c	K_d	Feed Water (ppm)	Product Water (ppm)	% Removal
	$(10^5 \cdot ft^2/hr)$					
1. Acetone	26.2	4.25	0.63	37.0	16.0	56.8
2. MEK	24.0	3.61	2.49	232	12.0	94.8
3. Benzene	24.0	3.61	407.	170	7.0	95.9
4. Phenol	23.3	3.44	0.70	23220	4590	80.2
5. o-Cresol	21.7	3.04	4.80	2040	50.0	97.5

Comments: 77 ppm of tert-butanol in product water.

Table G. Spray Column Data (Continued)

Spray column run # SS6B Temperature = 21.7°C

Dispersed phase = Isobutylene

Continuous phase = Lube oil refining waste water

V_d = 52.00 ft/hr, V_c = 21.56 ft/hr, F_s/F_w = 1.429

ρ_d = 0.5913 gm/cc, μ_d = 0.182 cp,

ρ_c = 0.9978 gm/cc, μ_c = 0.965 cp, σ = 41.5 dyne/cm

d_p = 0.1818 inch, ϕ = 0.0271, a = 10.72 ft^2/ft^3

Pe_c = 1.867, FF = 11.6%, RT = 6.56 seconds

Solute	D_d ($10^5 \cdot ft^2/hr$)	D_c ($10^5 \cdot ft^2/hr$)	K_d	Feed Water (ppm)	Product Water (ppm)	% Removal
1. Acetone	26.2	4.25	0.63	37.0	22.0	40.5
2. MEK	24.0	3.61	2.49	232	55.0	76.3
3. Benzene	24.0	3.61	407.	170	35.0	79.4
4. Phenol	23.3	3.44	0.70	23220	9550	58.9
5. o-Cresol	21.7	3.04	4.80	2040	328	83.9

Comments: 60 ppm of tert-butanol in product water.

Table G. Spray Column Data (Continued)

Spray column run # SS7 Temperature = 22.5°C

Dispersed phase = Isobutylene

Continuous phase = Prepared waste water

V_d = 67.95 ft/hr, V_c = 21.56 ft/hr, F_s/F_w = 1.867

ρ_d = 0.5911 gm/cc, μ_d = 0.180 cp,

ρ_c = 0.9977 gm/cc, μ_c = 0.947 cp, σ = 41.5 dyne/cm

d_p = 0.1844 inch, ϕ = 0.0362, a = 14.12 ft^2/ft^3

Pe_c = 2.091, FF = 13.8%, RT = 6.71 seconds

Solute	D_d ($10^5 \cdot ft^2/hr$)	D_c ($10^5 \cdot ft^2/hr$)	K_d	Feed Water (ppm)	Product Water (ppm)	% Removal
1. MEK	24.3	3.69	2.49	1972	440	77.7
2. Crotonal.	24.3	3.70	2.48	2094	482	77.0

Spray column run # SS8A Temperature = 21.8°C

Dispersed phase = Isobutylene

Continuous phase = Prepared waste water

V_d = 36.06 ft/hr, V_c = 15.36 ft/hr, F_s/F_w = 1.393

ρ_d = 0.5919 gm/cc, μ_d = 0.181 cp,

ρ_c = 0.9978 gm/cc, μ_c = 0.963 cp, σ = 41.6 dyne/cm

d_p = 0.1789 inch, ϕ = 0.0183, a = 7.37 ft^2/ft^3

Pe_c = 1.151, FF = 8.1%, RT = 6.40 seconds

Solute	D_d ($10^5 \cdot ft^2/hr$)	D_c ($10^5 \cdot ft^2/hr$)	K_d	Feed Water (ppm)	Product Water (ppm)	% Removal
1. Propionit.	25.7	3.93	1.80	4092	380	90.7
2. n-BuOH	23.5	3.34	0.76	6259	1344	78.5

Table G. Spray Column Data (Continued)

Spray column run # SS8B Temperature = 21.8°C

Dispersed phase = Isobutylene

Continuous phase = Prepared waste water

V_d = 67.95 ft/hr, V_c = 15.36 ft/hr, F_s/F_w = 2.624

ρ_d = 0.5919 gm/cc, μ_d = 0.181 cp,

ρ_c = 0.9978 gm/cc, μ_c = 0.963 cp, σ = 41.6 dyne/cm

d_p = 0.1847 inch, ϕ = 0.0360, a = 14.03 ft^2/ft^3

Pe_c = 1.482, FF = 12.5%, RT = 6.67 seconds

Solute	D_d ($10^5 \cdot ft^2/hr$)	D_c ($10^5 \cdot ft^2/hr$)	K_d	Feed Water (ppm)	Product Water (ppm)	% Removal
1. Propionit.	25.7	3.93	1.80	4092	161	96.1
2. n-BuOH	23.5	3.34	0.76	6259	742	88.1

Spray column run # SS9A Temperature = 22.7°C

Dispersed phase = Isobutylene

Continuous phase = Prepared waste water

V_d = 43.18 ft/hr, V_c = 51.27 ft/hr, F_s/F_w = 0.499

ρ_d = 0.5908 gm/cc, μ_d = 0.180 cp,

ρ_c = 0.9976 gm/cc, μ_c = 0.962 cp, σ = 41.5 dyne/cm

d_p = 0.1801 inch, ϕ = 0.0224, a = 8.97 ft^2/ft^3

Pe_c = 4.115, FF = 14.6%, RT = 6.54 seconds

Solute	D_d ($10^5 \cdot ft^2/hr$)	D_c ($10^5 \cdot ft^2/hr$)	K_d	Feed Water (ppm)	Product Water (ppm)	% Removal
1. EDC	24.6	3.69	70.0	3014	225	92.5
2. IAA	22.2	3.10	3.53	2472	717	71.0

Spray Column Data (Continued)

Spray column run # SS9B   Temperature = 22.7°C

Dispersed phase = Isobutylene

Continuous phase = Prepared Waste Water

V_d = 30.17 ft/hr, V_c = 51.27 ft/hr, F_s/F_w = 0.348

ρ_d = 0.5908 gm/cc, μ_d = 0.180 cp,

ρ_c = 0.9976 gm/cc, μ_c = 0.962 cp, σ = 41.5 dyne/cm

d_p = 0.1773 inch, ϕ = 0.0156, a = 6.33 ft^2/ft^3

Pe_c = 3.662, FF = 12.4%, RT = 6.51 seconds

Solute	D_d	D_c	K_d	Feed Water (ppm)	Product Water (ppm)	% Removal
	($10^5 \cdot ft^2/hr$)					
1. EDC	24.6	3.69	70.0	3014	659	78.1
2. IAA	22.2	3.10	3.53	2472	1169	52.7

Spray column run # SS9C   Temperature = 22.7°C

Dispersed phase = Isobutylene

Continuous phase =Prepared Waste Water

V_d = 17.17 ft/hr, V_c = 51.27 ft/hr, F_s/F_w = 0.198

ρ_d = 0.5908 gm/cc, μ_d = 0.180 cp,

ρ_c = 0.9976 gm/cc, μ_c = 0.962 cp, σ = 41.5 dyne/cm

d_p = 0.1740 inch, ϕ = 0.0089, a = 3.67 ft^2/ft^3

Pe_c = 3.072, FF = 9.7%, RT = 6.51 seconds

Solute	D_d	D_c	K_d	Feed Water (ppm)	Product Water (ppm)	% Removal
	($10^5 \cdot ft^2/hr$)					
1. EDC	24.6	3.69	70.0	3014	(48.3)	(98.4)
2. IAA	22.2	3.10	3.53	2472	1311	47.0

Comments: High EDC removal due to loss from sample bottle.

Table G. Spray Column Data (Continued)

Spray column run # SS10A Temperature = 23.4°C

Dispersed phase = n-Butane

Continuous phase = Prepared Waste Water

V_d = 43.77 ft/hr, V_c = 51.27 ft/hr, F_s/F_w = 0.475

ρ_d = 0.5549 gm/cc, μ_d = 0.197 cp,

ρ_c = 0.9974 gm/cc, μ_c = 0.927 cp, σ = 47.0 dyne/cm

d_p = 0.1817 inch, ϕ = 0.0217, a = 8.60 ft^2/ft^3

Pe_c = 3.852, FF = 14.1%, RT = 6.25 seconds

Solute	D_d	D_c	K_d	Feed Water (ppm)	Product Water (ppm)	% Removal
	($10^5 \cdot ft^2/hr$)					
1. EDC	22.5	3.84	44.0	2890	735	74.6
2. IAA	20.4	3.22	1.44	2063	1185	42.6

Spray column run # SS10B Temperature = 23.4°C

Dispersed phase = n-Butane

Continuous phase = Prepared Waste Water

V_d = 31.40 ft/hr, V_c = 51.27 ft/hr, F_s/F_w = 0.341

ρ_d = 0.5549 gm/cc, μ_d = 0.197 cp,

ρ_c = 0.9974 gm/cc, μ_c = 0.927 cp, σ = 47.0 dyne/cm

d_p = 0.1792 inch, ϕ = 0.0155, a = 6.24 ft^2/ft^3

Pe_c = 3.468, FF = 12.0%, RT = 6.24 seconds

Solute	D_d	D_c	K_d	Feed Water (ppm)	Product Water (ppm)	% Removal
	($10^5 \cdot ft^2/hr$)					
1. EDC	22.5	3.84	44.0	2890	1181	59.1
2. IAA	20.4	3.22	1.44	2063	1457	29.4

Table G. Spray Column Data (Continued)

Spray column run # SS10C Temperature = 23.4°C

Dispersed phase = n-Butane

Continuous phase = Prepared Waste Water

V_d = 17.42 ft/hr, V_c = 51.27 ft/hr, F_s/F_w = 0.189

ρ_d = 0.5549 gm/cc, μ_d = 0.197 cp,

ρ_c = 0.9974 gm/cc, μ_c = 0.927 cp, σ = 47.0 dyne/cm

d_p = 0.1759 inch, ϕ = 0.0086, a = 3.53 ft^2/ft^3

Pe_c = 2.883, FF = 9.2%, RT = 6.24 seconds

Solute	D_d	D_c	K_d	Feed Water (ppm)	Product Water (ppm)	% Removal
	($10^5\cdot ft^2/hr$)					
1. EDC	22.5	3.84	44.0	2890	1657	42.7
2. IAA	20.4	3.22	1.44	2063	1668	19.1

Spray column run # SS11A Temperature = 21.4°C

Dispersed phase = Isobutylene

Continuous phase = Prepared Waste Water

V_d = 43.18 ft/hr, V_c = 36.80 ft/hr, F_s/F_w = 0.697

ρ_d = 0.5924 gm/cc, μ_d = 0.182 cp,

ρ_c = 0.9979 gm/cc, μ_c = 0.972 cp, σ = 41.7 dyne/cm

d_p = 0.1806 inch, ϕ = 0.0222, a = 8.87 ft^2/ft^3

Pe_c = 2.935, FF = 12.8%, RT = 6.49 seconds

Solute	D_d	D_c	K_d	Feed Water (ppm)	Product Water (ppm)	% Removal
	($10^5\cdot ft^2/hr$)					
1. EDC	24.2	3.64	70.0	2892	370	87.2

Table G. Spray Column Data (Continued)

Spray column run # SS11B Temperature = 21.4°C
Dispersed phase = Isobutylene
Continuous phase = Prepared Waste Water
V_d = 17.17 ft/hr, V_c = 36.80 ft/hr, F_s/F_w = 0.277
ρ_d = 0.5924 gm/cc, μ_d = 0.182 cp,
ρ_c = 0.9979 gm/cc, μ_c = 0.972 cp, σ = 41.7 dyne/cm
d_p = 0.1744 inch, ϕ = 0.0088, a = 3.63 ft^2/ft^3
Pe_c = 2.191, FF = 8.0%, RT = 6.46 seconds

Solute	D_d	D_c	K_d	Feed Water (ppm)	Product Water (ppm)	% Removal
	$(10^5 \cdot ft^2/hr)$					
1. EDC	24.2	3.64	70.0	2892	1098	62.0

Spray column run # SS12A Temperature = 21.6°C
Dispersed phase = Isobutylene
Continuous phase = Prepared Waste Water
V_d = 52.25 ft/hr, V_c = 23.26 ft/hr, F_s/F_w = 1.331
ρ_d = 0.5914 gm/cc, μ_d = 0.182 cp,
ρ_c = 0.9979 gm/cc, μ_c = 0.970 cp, σ = 41.5 dyne/cm
d_p = 0.1819 inch, ϕ = 0.0272, a = 10.78 ft^2/ft^3
Pe_c = 2.017, FF = 11.9%, RT = 6.56 seconds

Solute	D_d	D_c	K_d	Feed Water (ppm)	Product Water (ppm)	% Removal
	$(10^5 \cdot ft^2/hr)$					
1. Acetone	26.2	4.22	0.63	2058	1307	36.5
2. MEK	24.0	3.87	2.49	4167	1579	62.1
3. Crotonal.	24.0	3.88	2.48	4422	1620	63.4
4. n-BuAc	20.4	2.71	168.0	2212	620	72.0

Table G. Spray Column Data (Continued)

Spray column run # SS12B Temperature = 21.6°C

Dispersed phase = Isobutylene

Continuous phase = Prepared Waste Water

V_d = 83.16 ft/hr, V_c = 23.26 ft/hr, F_s/F_w = 2.189

ρ_d = 0.5914 gm/cc, μ_d = 0.182 cp,

ρ_c = 0.9979 gm/cc, μ_c = 0.970 cp, σ = 41.5 dyne/cm

d_p = 0.1868 inch, ϕ = 0.0447, a = 17.24 ft^2/ft^3

Pe_c = 2.435, FF = 16.3%, RT = 6.78 seconds

Solute	D_d ($10^5 \cdot ft^2/hr$)	D_c ($10^5 \cdot ft^2/hr$)	K_d	Feed Water (ppm)	Product Water (ppm)	% Removal
1. Acetone	26.2	4.22	0.63	2058	1090	47.0
2. MEK	24.0	3.87	2.49	4167	1084	74.0
3. Crotonal.	24.0	3.88	2.48	4422	1152	74.0
4. n-BuAc	20.4	2.71	168.0	2212	431	80.5

Spray column run # SS13A Temperature = 21.6°C

Dispersed phase = Isobutylene

Continuous phase = Prepared Waste Water

V_d = 52.25 ft/hr, V_c = 23.26 ft/hr, F_s/F_w = 1.333

ρ_d = 0.5922 gm/cc, μ_d = 0.182 cp,

ρ_c = 0.9979 gm/cc, μ_c = 0.967 cp, σ = 41.7 dyne/cm

d_p = 0.1822 inch, ϕ = 0.0272, a = 10.75 ft^2/ft^3

Pe_c = 2.013, FF = 12.0%, RT = 6.56 seconds

Solute	D_d ($10^5 \cdot ft^2/hr$)	D_c ($10^5 \cdot ft^2/hr$)	K_d	Feed Water (ppm)	Product Water (ppm)	% Removal
1. Acetone	26.2	4.24	0.63	2099	539	74.3
2. Benzene	24.0	3.60	407.	300.7	5.7	98.1
3. n-BuOH	23.4	3.44	0.76	4174	924	77.9
4. n-BuAc	20.4	2.73	168.	2067	6.7	99.7

Table G. Spray Column Data (Continued)

Spray column run # SS13B Temperature = 20.7°C

Dispersed phase = Isobutylene

Continuous phase = Prepared Waste Water

V_d = 26.86 ft/hr, V_c = 23.26 ft/hr, F_s/F_w = 0.686

ρ_d = 0.5933 gm/cc, μ_d = 0.183 cp,

ρ_c = 0.9981 gm/cc, μ_c = 0.988 cp, σ = 41.9 dyne/cm

d_p = 0.1774 inch, ϕ = 0.0137, a = 5.54 ft^2/ft^3

Pe_c = 1.581, FF = 8.0%, RT = 6.40 seconds

Solute	D_d	D_c	K_d	Feed Water (ppm)	Product Water (ppm)	% Removal
	($10^5 \cdot ft^2/hr$)					
1. Acetone	25.9	4.15	0.63	2072	1492	28.0
2. Benzene	23.8	3.53	407.	288.3	20.0	93.1
3. n-BuOH	23.2	3.36	0.76	4122	2667	35.3
4. n-BuAc	20.3	2.67	168.	2110	197	90.7

Table G. Spray Column Data (Continued)

Spray column run # SS14 Temperature = 21.6°C

Dispersed phase = Isobutylene

Continuous phase = Cresylic Acid Recovery Waste Water

V_d = 60.59 ft/hr, V_c = 20.14 ft/hr, F_s/F_w = 1.785

ρ_d = 0.5922 gm/cc, μ_d = 0.182 cp,

ρ_c = 0.9979 gm/cc, μ_c = 0.967 cp, σ = 41.7 dyne/cm

d_p = 0.1837 inch, ϕ = 0.0319, a = 12.50 ft^2/ft^3

Pe_c = 1.853, FF = 12.5%, RT = 6.63 seconds

Solute	D_d ($10^5 \cdot ft^2/hr$)	D_c ($10^5 \cdot ft^2/hr$)	K_d	Feed Water (ppm)	Product Water (ppm)	% Removal
1. Phenol	23.3	3.43	0.70	579	163	71.8
2. o-Cresol	21.7	3.01	4.80	307	31.2	89.8
3. m, p-Cresol	21.7	3.01	2.70	291	25.2	91.3
4. Xylenols	20.4	2.71	7.0	227	10.0	95.6

Comments: Feed Water COD = 4050;
Product Water COD = 1070.

Table G. Spray Column Data (Continued)

Spray column run # SS15A Temperature = 21.3°C
Dispersed phase = Isobutylene
Continuous phase = Prepared Waste Water
V_d = 52.25 ft/hr, V_c = 23.26 ft/hr, F_s/F_w = 1.334
ρ_d = 0.5926 gm/cc, μ_d = 0.182 cp,
ρ_c = 0.9979 gm/cc, μ_c = 0.974 cp, σ = 41.7 dyne/cm
d_p = 0.1823 inch, ϕ = 0.0272, a = 10.74 ft^2/ft^3
Pe_c = 2.011, FF = 12.0%, RT = 6.56 seconds

Solute	D_d	D_c	K_d	Feed Water (ppm)	Product Water (ppm)	% Removal
	($10^5 \cdot ft^2/hr$)					
1. Acetone	26.1	4.21	0.63	2049	590	71.2
2. n-BuAc	20.4	2.70	168.	2113	11.8	99.4

Spray column run # SS15B Temperature = 21.3°C
Dispersed phase = Isobutylene
Continuous phase = Prepared Waste Water
V_d = 26.86 ft/hr, V_c = 23.26 ft/hr, F_s/F_w = 0.686
ρ_d = 0.5926 gm/cc, μ_d = 0.182 cp,
ρ_c = 0.9979 gm/cc, μ_c = 0.974 cp, σ = 41.7 dyne/cm
d_p = 0.1770 inch, ϕ = 0.0137, a = 5.56 ft^2/ft^3
Pe_c = 1.588, FF = 8.0%, RT = 6.42 seconds

Solute	D_d	D_c	K_d	Feed Water (ppm)	Product Water (ppm)	% Removal
	($10^5 \cdot ft^2/hr$)					
1. Acetone	26.1	4.21	0.63	2049	1341	34.6
2. n-BuAc	20.4	2.70	168.	2113	144	93.2

Table G. Spray Column Data (Continued)

Spray column run # SS16 Temperature = 22.7°C
Dispersed phase = Isobutylene
Continuous phase = Prepared Waste Water
V_d = 52.25 ft/hr, V_c = 23.26 ft/hr, F_s/F_w = 1.330
ρ_d = 0.5908 gm/cc, μ_d = 0.180 cp,
ρ_c = 0.9976 gm/cc, μ_c = 0.942 cp, σ = 41.5 dyne/cm
d_p = 0.1818 inch, ϕ = 0.0273, a = 10.81 ft^2/ft^3
Pe_c = 2.026, FF = 11.9%, RT = 6.58 seconds

Solute	D_d	D_c	K_d	Feed Water (ppm)	Product Water (ppm)	% Removal
	$(10^5 \cdot ft^2/hr)$					
1. Acetone	26.6	4.37	0.63	1986	1093	45.0
2. MEK	24.3	3.71	2.49	3957	1257	68.2
3. Crotonal.	24.4	3.72	2.48	4247	1373	67.7
4. n-BuAc	20.7	2.81	168.	2138	508	76.2

Spray column run # SW1A Temperature = 20.0°C
Dispersed phase = Prepared Waste Water
Continuous phase = Isobutylene
V_d = 51.27 ft/hr, V_c = 17.17 ft/hr, F_s/F_w = 0.199
ρ_d = 0.9982 gm/cc, μ_d = 1.005 cp,
ρ_c = 0.5942 gm/cc, μ_c = 0.184 cp, σ = 42.0 dyne/cm
d_p = 0.1947 inch, ϕ = 0.0233, a = 8.62 ft^2/ft^3
Pe_c = 1.153, FF = 12.9%, RT = 5.73 seconds

Solute	D_d	D_c	K_d	Feed Water (ppm)	Product Water (ppm)	% Removal
	$(10^5 \cdot ft^2/hr)$					
1. EDC	3.50	23.8	70.0	2763	1129	59.1
2. IAA	2.94	21.6	3.53	1920	1327	30.9

Table G. Spray Column Data (Continued)

Spray column run # SW1B Temperature = 20.0°C
Dispersed phase = Prepared Waste Water
Continuous phase = Isobutylene
V_d = 51.27 ft/hr, V_c = 43.18 ft/hr, F_s/F_w = 0.501
ρ_d = 0.9982 gm/cc, μ_d = 1.005 cp,
ρ_c = 0.5942 gm/cc, μ_c = 0.184 cp, σ = 42.0 dyne/cm
d_p = 0.1947 inch, ϕ = 0.0236, a = 8.72 ft^2/ft^3
Pe_c = 2.912, FF = 16.1%, RT = 5.80 seconds

Solute	D_d	D_c	K_d	Feed Water (ppm)	Product Water (ppm)	% Removal
	($10^5\cdot ft^2/hr$)					
1. EDC	3.50	23.8	70.0	2763	860	68.9
2. IAA	2.94	21.6	3.53	1920	1076	44.0

Spray column run # SW2A Temperature = 18.6°C
Dispersed phase = Prepared Waste Water
Continuous phase = Isobutylene
V_d = 36.80 ft/hr, V_c = 43.18 ft/hr, F_s/F_w = 0.700
ρ_d = 0.9985 gm/cc, μ_d = 1.040 cp,
ρ_c = 0.5960 gm/cc, μ_c = 0.186 cp, σ = 42.3 dyne/cm
d_p = 0.1935 inch, ϕ = 0.0168, a = 6.24 ft^2/ft^3
Pe_c = 2.572, FF = 12.8%, RT = 5.74 seconds

Solute	D_d	D_c	K_d	Feed Water (ppm)	Product Water (ppm)	% Removal
	($10^5\cdot ft^2/hr$)					
1. EDC	3.37	23.4	70.0	3061	537	82.5
2. n-BuOH	3.17	22.7	0.76	2065	1546	25.1
3. n-BuAc	2.51	19.8	168.	2184	456	79.1

Table G. Spray Column Data (Continued)

Spray column run # SW2B Temperature = 18.6°C

Dispersed phase = Prepared Waste Water

Continuous phase = Isobutylene

V_d = 36.80 ft/hr, V_c = 30.17 ft/hr, F_s/F_w = 0.489

ρ_d = 0.9985 gm/cc, μ_d = 1.040 cp,

ρ_c = 0.5960 gm/cc, μ_c = 0.186 cp, σ = 42.3 dyne/cm

d_p = 0.1936 inch, ϕ = 0.0167, a = 6.20 ft^2/ft^3

Pe_c = 1.793, FF = 11.5%, RT = 5.71 seconds

Solute	D_d	D_c	K_d	Feed Water	Product Water	% Removal
	($10^5 \cdot ft^2/hr$)			(ppm)	(ppm)	
1. EDC	3.37	23.4	70.0	3061	605	80.2
2. n-BuOH	3.17	22.7	0.76	2065	1581	23.4
3. n-BuAc	2.51	19.8	168.	2184	547	75.0

Spray column run # SW2C Temperature = 18.6°C

Dispersed phase = Prepared Waste Water

Continuous phase = Isobutylene

V_d = 27.23 ft/hr, V_c = 30.17 ft/hr, F_s/F_w = 0.661

ρ_d = 0.9985 gm/cc, μ_d = 1.040 cp,

ρ_c = 0.5960 gm/cc, μ_c = 0.186 cp, σ = 42.3 dyne/cm

d_p = 0.1909 inch, ϕ = 0.0123, a = 4.65 ft^2/ft^3

Pe_c = 1.637, FF = 9.3%, RT = 5.71 seconds

Solute	D_d	D_c	K_d	Feed Water	Product Water	% Removal
	($10^5 \cdot ft^2/hr$)			(ppm)	(ppm)	
1. EDC	3.37	23.4	70.0	3061	519	83.0
2. n-BuOH	3.17	22.7	0.76	2065	1507	27.0
3. n-BuAc	2.51	19.8	168.	2184	473	78.3

Table G. Spray Column Data (Continued)

Spray column run # SW3A Temperature = 18.3°C

Dispersed phase = Prepared Waste Water

Continuous phase = Isobutylene

V_d = 36.80 ft/hr, V_c = 43.18 ft/hr, F_s/F_w = 0.701

ρ_d = 0.9985 gm/cc, μ_d = 1.048 cp,

ρ_c = 0.5963 gm/cc, μ_c = 0.187 cp, σ = 42.3 dyne/cm

d_p = 0.1936 inch, ϕ = 0.0168, a = 6.24 ft^2/ft^3

Pe_c = 2.571, FF = 12.8%, RT = 5.74 seconds

Solute	D_d	D_c	K_d	Feed Water (ppm)	Product Water (ppm)	% Removal
	$(10^5 \cdot ft^2/hr)$					
1. EDC	3.34	23.3	70.0	3128	1529	51.1

Spray column run # SW3B Temperature = 18.3°C

Dispersed phase = Prepared Waste Water

Continuous phase = Isobutylene

V_d = 36.80 ft/hr, V_c = 30.17 ft/hr, F_s/F_w = 0.490

ρ_d = 0.9985 gm/cc, μ_d = 1.048 cp,

ρ_c = 0.5963 gm/cc, μ_c = 0.187 cp, σ = 42.3 dyne/cm

d_p = 0.1936 inch, ϕ = 0.0167, a = 6.20 ft^2/ft^3

Pe_c = 1.793, FF = 11.5%, RT = 5.71 seconds

Solute	D_d	D_c	K_d	Feed Water (ppm)	Product Water (ppm)	% Removal
	$(10^5 \cdot ft^2/hr)$					
1. EDC	3.34	23.3	70.0	3128	1501	52.0

Table G. Spray Column Data (Continued)

Spray column run # SW3C   Temperature = 18.3°C

Dispersed phase = Prepared Waste Water

Continuous phase = Isobutylene

V_d = 36.80 ft/hr, V_c = 17.17 ft/hr, F_s/F_w = 0.279

ρ_d = 0.9985 gm/cc, μ_d = 1.048 cp,

ρ_c = 0.5963 gm/cc, μ_c = 0.187 cp, σ = 42.3 dyne/cm

d_p = 0.1936 inch, ϕ = 0.0166, a = 6.16 ft^2/ft^3

Pe_c = 1.018, FF = 9.9%, RT = 5.67 seconds

Solute	D_d	D_c	K_d	Feed Water (ppm)	Product Water (ppm)	% Removal
	($10^5 \cdot ft^2/hr$)					
1. EDC	3.34	23.3	70.0	3128	1535	50.9

Spray column run # SW3E   Temperature = 18.3°C

Dispersed phase = Prepared Waste Water

Continuous phase = Isobutylene

V_d = 27.23 ft/hr, V_c = 30.17 ft/hr, F_s/F_w = 0.662

ρ_d = 0.9985 gm/cc, μ_d = 1.048 cp,

ρ_c = 0.5963 gm/cc, μ_c = 0.187 cp, σ = 42.3 dyne/cm

d_p = 0.1910 inch, ϕ = 0.0123, a = 4.65 ft^2/ft^3

Pe_c = 1.637, FF = 9.3%, RT = 5.71 seconds

Solute	D_d	D_c	K_d	Feed Water (ppm)	Product Water (ppm)	% Removal
	($10^5 \cdot ft^2/hr$)					
1. EDC	3.34	23.3	70.0	3128	1406	55.1

Table G. Spray Column Data (Continued)

Spray column run # SW3E Temperature = 18.3°C

Dispersed phase = Prepared Waste Water

Continuous phase = Isobutylene

V_d = 27.23 ft/hr, V_c = 43.18 ft/hr, F_s/F_w = 0.947

ρ_d = 0.9985 gm/cc, μ_d = 1.048 cp,

ρ_c = 0.5963 gm/cc, μ_c = 0.187 cp, σ = 42.3 dyne/cm

d_p = 0.1910 inch, ϕ = 0.0124, a = 4.68 ft^2/ft^3

Pe_c = 2.347, FF = 10.5%, RT = 5.74 seconds

Solute	D_d ($10^5 \cdot ft^2/hr$)	D_c ($10^5 \cdot ft^2/hr$)	K_d	Feed Water (ppm)	Product Water (ppm)	% Removal
1. EDC	3.34	23.3	70.0	3128	1395	55.4

APPENDIX H

EXPERIMENTAL DATA FROM RDC EXTRACTOR

The data which were directly determined at steady state in each run conducted in the RDC extractor included the solvent and water flow rates, the diameters of the discs and stator holes, the compartment heights and whole column height, the rotational speed of the discs, the temperatures of the two streams leaving the RDC, and the concentrations of each solute in the feed and product water. In some experiments the solvent hold-up and the solute concentrations in the loaded solvent were also measured. Since the difference between the two temperature measurements was less than 1°C, the average was taken as the column temperature. These experimental data were then combined with estimates for physical properties to compute experimental mass transfer coefficients. Since these calculations were lengthy and repetitious, a computer program was developed and used. In this appendix the calculational procedure and computer programs are described, then the results for 15 runs conducted in the RDC extractor are listed.

Estimates of Physical Properties.

The aqueous phase density and viscosity at the column temperature were taken as those listed by Weast (1970) for pure water. The density and viscosity for the volatile solvent phases were determined from data listed for the pure solvents (API, 1963). The interfacial tensions were estimated by the method of Donahue and Bartell (1952) as discussed in Section VII. The density and viscosity for n-butyl acetate were from Toropov (1956). The interfacial tension at 20°C was taken from Logsdail, et al. (1957), and the correlation of Donahue and Bartell (1952) was used to correct this value to the column temperature. For mixtures of n-butyl acetate and isobutylene, the density was estimated by assuming no excess volume of mixing, the viscosity was estimated from the molar average of $\ln \mu_i$, and the interfacial tension was estimated from the molar average of σ_i, where μ_i and σ_i are for pure components. The density and viscosity of 2-ethyl hexanol were taken from Marks (1967). The interfacial tension was assumed equal to that for n-octanol as given by Weast (1970).

The diffusivities for each solute in water and in the solvent were estimated by the method of Scheibel (1954) assuming that the values at infinite dilution would apply.

Computer Programs.

The majority of RDC extractor data reduction was done in the Fortran program EXPTRDC and subprograms RDC and POFUNC. Program EXPTRDC begins by reading in the superficial velocities of each phase, VD and VC, the column temperature, TEMP, the rotational speed, RPM, the measured hold-up, PHI, and the column dimensions including disc diameter, DI, stator hole diameter, DS, column diameter, DC, compartment height, HC, and column height, COLHT. When the hold-up was not measured or when G_{18} is assumed for some other reason, the value read into PHI is $(1 + G_{18})$. The program senses that PHI is greater than 1 so that the correct value for PHI must be calculated using G_{18}. All physical properties are next read in. The subroutine RDC is called to make all design calculations for the RDC extractor. Program EXPTRDC then prints out the results.

Subroutine RDC uses data stored in various common blocks to design the RDC. It first calculates PHI or G18, depending upon which is specified and which must be calculated, using the correlation of Strand, et al. (1962). This step includes the calculation of drop diameter, DP, slip velocity, VS, and power per unit mass, POM. The function subprogram POFUNC is used during this calculation to determine the power number using the disc Reynolds number, RE, after the correlation of Reman and van der Vusse (1955).

Subroutine RDC continues by checking for flooding both by the correlation of Logsdail, et al. (1957) and by the method of Strand, et al. (1962). The two Peclet numbers, PEC and PED, are calculated using the equations developed in Appendix B. The calculations in RDC are completed by determining theoretical estimates for the solvent-phase number of transfer units, NS, for the water-phase number of transfer units, NW, and for the overall water-phase number of transfer units, NOW. The interfacial area per unit of extractor volume, A, and the solvent droplet rise time, R, are calculated. Theoretical estimates for NOW are made for stagnant drops and for circulating drops using the equations of Strand, et al. (1962). Theoretical estimates are made for NW using the model of Calderbank and Moo-Young (1961). This estimate is then used with NS calculated for stagnant drops to calculate a third estimate for NOW.

The final step in determining the experimental values for the overall water-phase number of transfer units was accomplished using the program EVAL and subroutines FINDN and EETA. These programs were listed in Appendix G. The values of PEC and PED determined in RDC are read in. A value of E, the extraction factor, and ZETA [η in equation (1), calculated using measured concentrations] is read into EVAL for each component. By using the search subroutine FINDN, equation (3) is solved implicitly to determine NOW for each component.

A listing of the program follows. At the end a typical output is shown for run KS13.

PROGRAM EXPTRDC

```
      PROGRAM EXPTRDC(INPUT,OUTPUT)
C* EXPTRDC ACCEPTS DATA FROM AN EXPERIMENTAL RUN AND CALLS FOR THE
C*** THE CALCULATION OF DROP DIAMETER, PECLET NUMBERS, AND MASS TRANSFER
C*** COEFFICIENTS.
      COMMON/DIMEN/DI,DS,DC,HC,COLHT,CR
      COMMON/PROPS/DENSD,DENSC,DELDEN,SIGMA,VISCD,VISCC,NCOMPS,
     1  DIFFD(6),DIFFC(6),KD(6)
      COMMON/OPERAT/VD,VC,RPM,PE,POM,PHI,G18,DP,DPT,OSCFACT,A,R
      COMMON/BMEMT/PED,PEC,PHIF,VK,FFS,VKL,FFL,ETA(6),E(6),NWSTAG(6),
     1  NSSTAG(6),NOWSTAG(6),NWCIRC(6),NSCIRC(6),NOWCIRC(6),NWTURB(6),
     2  NSTURB(6),NOWTURB(6)
      REAL KD,NWSTAG,NSSTAG,NOWSTAG,NWCIRC,NSCIRC,NOWCIRC,NWTURB,NSTURB,
     1  NOWTURB
      LOGICAL FLOOD,CALCPHI
      DIMENSION NAME(6),PPMF(6),PPMP(6)
C*** BEGIN FORMAT STATEMENTS ********************************************
    1 FORMAT(A5,1X,I1,F8.4,F10.4,F5.1,F10.1,F10.6,4F5.2,F7.3,I3)
    2 FORMAT(2F10.5,F10.3,2F10.4)
    3 FORMAT(A8,2X,3F10.2)
    6 FORMAT(1H1,20X,36HANALYSIS  OF  RDC  EXTRACTION  RUN  ,A5,8X,
     1  6HPAGE 1///14X,29H**** EXPERIMENTAL CONDITIONS/23X,
     2  27HVELOCITY DISPERSED PHASE = ,F6.3,6H FT/HR/23X,28HVELOCITY CON
     3TINUOUS PHASE = ,F6.3,6H FT/HR/23X,14HTEMPERATURE = ,F4.1,
     4  10H DEGREES C/23X,19HROTATIONAL SPEED = ,F6.1,4H RPM,/23X,
     5 10HHOLD-UP = ,F7.6,4X,10H(MEASURED)/23X,6HG18 = ,F7.4,8X,
     6 12H(CALCULATED)///14X,22H**** COLUMN DIMENSIONS/23X,
     7  16HDISC DIAMETER = ,F5.2,5H INCH/23X,23HSTATOR HOLE DIAMETER = ,
     8  F5.2,5H INCH/23X,18HCOLUMN DIAMETER = ,F5.2,5H INCH/23X,
     9  21HCOMPARTMENT HEIGHT = ,F5.2,5H INCH/23X,16HCOLUMN HEIGHT = ,
     1  F7.3,5H INCH//)
    7 FORMAT(1H1,20X,35HANALYSIS  OF  RDC  EXTRACTION  RUN  ,A5,8X,
     1  6HPAGE 1///14X,28H**** EXPERIMENTAL CONDITIONS/23X,
     2  27HVELOCITY DISPERSED PHASE = ,F6.3,6H FT/HR/23X,28HVELOCITY CON
     3TINUOUS PHASE = ,F6.3,6H FT/HR/23X,14HTEMPERATURE = ,F4.1,
     4  10H DEGREES C/23X,19HROTATIONAL SPEED = ,F6.1,4H RPM,/23X,
     5 10HHOLD-UP = ,F7.6,4X,12H(CALCULATED)/23X,6HG18 = ,F7.4,8X,
     6  11H(ESTIMATED)///14X,22H**** COLUMN DIMENSIONS/23X,
     7  16HDISC DIAMETER = ,F5.2,5H INCH/23X,23HSTATOR HOLE DIAMETER = ,
     8  F5.2,5H INCH/23X,18HCOLUMN DIAMETER = ,F5.2,5H INCH/23X,
     9  21HCOMPARTMENT HEIGHT = ,F5.2,5H INCH/23X,16HCOLUMN HEIGHT = ,
     1  F7.3,5H INCH//)
    8 FORMAT(14X,24H**** PHYSICAL PROPERTIES/23X,26HDENSITY DISPERSED PH
     1ASE = ,F7.5,8H GRAM/CC/23X,27HDENSITY CONTINUOUS PHASE = ,F7.5,
     28H GRAM/CC/23X,22HINTERFACIAL TENSION = ,F7.2,8H DYNE/CM/23X,
     328HVISCOSITY DISPERSED PHASE = ,F7.4,3H CP/23X,
     429HVISCOSITY CONTINUOUS PHASE = ,F7.3,3H CP//)
    9 FORMAT(14X,29H**** FLOODING CHARACTERISTICS/23X,8HVD/VC = ,F7.5,/
     1  23X,15HPHI FLOODING = ,F7.6,/23X,16HVK (LOGSDAIL) = ,F7.2,
     2  6H FT/HR/23X,27HFRACTION OF FLOODING (L) = ,F5.4,/23X,
     3  14HVK (STRAND) = ,F7.2,6H FT/HR/23X,27HFRACTION OF FLOODING (S)
     4= ,F5.4,/23X,16HDROP DIAMETER = ,F7.6,5H INCH/23X,22HTRANSITION DR
     5OP DIA = ,F7.6,5H INCH/23X,17HPOWER PER MASS = ,F7.2,
     6  14H FT-LBF/HR-LBM/23X,21HOSCILLATION FACTOR = ,F7.4//)
```

```
   10 FORMAT(14X,33H**** AXIAL MIXING CHARACTERISTICS/23X,
     1/23X,6HPEC = ,F8.4//)
   11 FORMAT(1H1,20X,36HANALYSIS  OF  RDC  EXTRACTION  RU
     1  6HPAGE 2///14X,62H*** SOLUTE DIFFUSIVITIES, DIST
     2CIENTS, AND E(I)/28X,15H10**5 * SQFT/HR/17X,6HSOLUT
     3  5X,5HDC(I),11X,5HKD(I),9X,4HE(I)/)
   12 FORMAT(16X,A8,F9.2,F10.2,F16.2,F1[illegible].2)
   13 FORMAT(1H0/14X,28H**** MASS TRANSFER ESTIMATES/23X,
     1  10H SQFT/CUFT/23X,12HRISE TIME = ,1PE10.3,3H HR)
   14 FORMAT(1H0,14X,17H** STAGNANT DROPS/17X,6HSOLUTE,9X,
     1  8X,3HNOW/)
   15 FORMAT(16X,A8,2X,3F10.3)
   16 FORMAT(1H0,14X,20H** CIRCULATING DROPS/17X,6HSOLUTE,
     1  2HNS,8X,3HNOW/)
   17 FORMAT(1H0,14X,18H** TURBULENT DROPS/17X,6HSOLUTE,
     1  8X,3HNOW/)
   18 FORMAT(1H0/14X,26H**** EXPERIMENTAL REMOVALS/17X,6H
     1  8HFEED PPM,4X,8HPROD PPM,7X,3HETA/)
   19 FORMAT(10X,2F10.1)
   20 FORMAT(1HX,15X,A8,F11.1,F12.1,F12.5)
C*** END OF FORMAT STATEMENTS ****************************
C*** READ IN EXPERIMENTAL CONDITIONS
   31 READ 1,RUNNUM,JUMP,VD,VC,TEMP,RPM,PHI,DI,DS,DC,HC,
      IF(VD.EQ. 0.0) GO TO 100
      CALCPHI = .FALSE.
      IF(PHI .GT. 1.0) CALCPHI = .TRUE.
      IF(JUMP.EQ.1) GO TO 36
C*** READ IN PHYSICAL PROPERTY DATA (GM/CC,GM/CC,DYNE/CM,
      READ 2,DENSD,DENSC,SIGMA,VISCD,VISCC
      DELDEN = ABS(DENSD - DENSC)
C*** READ IN DIFFUSIVITIES
      DO 35 I=1,NCOMPS
C***           (-,10**5*SQFT/HR,10**5*SQFT/HR,-)
   35 READ 3,NAME(I),DIFFD(I),DIFFC(I),KD(I)
C*** CALL FOR RDC DESIGN
   36 CALL RDC(0,FLOOD,0,1,0,1,0)
C*** PRINT OPERATING CONDITIONS
      IF(CALCPHI) GO TO 40
      PRINT 6,RUNNUM,VD,VC,TEMP,RPM,PHI,G18,DI,DS,DC,HC,
      GO TO 41
   40 PRINT 7,RUNNUM,VD,VC,TEMP,RPM,PHI,G18,DI,DS,DC,HC,
C*** PRINT PHYSICAL PROPERTIES
   41 PRINT 8,DENSD,DENSC,SIGMA,VISCD,VISCC
C*** PRINT FLOODING CHARACTERISTICS
      AA = VD/VC
      AB = 2.392E-09*POW
      PRINT 9,AA,PHIF,VKL,FFL,VK,FFS,DP,DPT,AB,OSCFACT
C*** PRINT AXIAL MIXING PARAMETERS
      PRINT 10,PED,PEC
C*** PRINT SOLUTE DIFFUSIVITIES, DISTRIBUTION COEFFICIENT
      PRINT 11,RUNNUM
      DO 45 I=1,NCOMPS
   45 PRINT 12,NAME(I),DIFFD(I),DIFFC(I),KD(I),E(I)
C*** PRINT MASS TRANSFER RESULTS
      PRINT 13,A,R
      PRINT 14
      DO 46 I=1,NCOMPS
   46 PRINT 15.NAME(I).NWSTAG(I).NSSTAG(I).NOWSTAG(I)
      PRINT 16
      DO 47 I=1.NCOMPS
   47 PRINT 15.NAME(I).NWCIRC(I).NSCIRC(I).NOWCIRC(I)
      PRINT 17
      DO 48 I=1.NCOMPS
   48 PRINT 15.NAME(I).NWTURB(I).NSTURB(I).NOWTURB(I)
C*** READ IN AND PRINT EXPERIMENTAL REMOVAL EFFICIENCIES
      PRINT 18
      DO 50 I=1.NCOMPS
      IF(JUMP.EQ.1) GO TO 50
      READ 19.PPMF(I).PPMP(I)
      ETA(I) = PPMP(I)/PPMF(I)
   50 PRINT 20.NAME(I).PPMF(I).PPMP(I).ETA(I)
      GO TO 31
  100 CONTINUE
      END EXPTRDC
```

SUBROUTINE RDC

```
      SUBROUTINE RDC(KEY,FLOOD,MTTYPE,ANW,ANS)
C* RDC USES DATA STORED IN COMMONS TO DESIGN AN RDC EXTRACTOR
      COMMON/DIMEN/DI,DS,DC,HC,COLHT,CR
      COMMON/PROPS/DENSD,DENSC,DELDEN,SIGMA,VISCD,VISCC,NCOMPS,
     1  DIFFD(6),DIFFC(6),KD(6)
      COMMON/OPERAT/VD,VC,RPM,RE,POM,PHI,G18,DP,DPT,OSCFACT,A,R
      COMMON/BMFMT/PED,PEC,PHIF,VK,FFS,VKL,FFL,ETA(6),E(6),NWSTAG(6),
     1  NSSTAG(6),NOWSTAG(6),NWCIRC(6),NSCIRC(6),NOWCIRC(6),NWTURB(6),
     2  NSTURB(6),NOWTURB(6)
      REAL KD,NWSTAG,NSSTAG,NOWSTAG,NWCIRC,NSCIRC,NOWCIRC,NWTURB,NSTURB,
     1  NOWTURB,NOX
      DIMENSION Z(9),UA(101),UB(101)
      LOGICAL FLOOD
    1 FORMAT(1H0,45H**** **** **** PHI LOOP DID NOT CONVERGE ****//)
      FLOOD = .FALSE.
      AA = VD/VC
      PHIF = (SQRT(AA*AA + 8.0*AA) - 3.0*AA)/4.0/(1.0 - AA)
      VKF = (VC/(1.0 - PHIF) + VD/PHIF)/(1.0 - PHIF)
      AA = 1.0 - (DI/DC)**2
      AB = (DS/DC)**2
      AC = ((DS + DI)/DC)*SQRT(((DS - DI)/DC)**2 + (HC/DC)**2)
      CR = AMIN1(AA,AB,AC)
      IF(KEY.EQ.1) GO TO 10
C*** IF KEY.NE.1, CALCULATE PARAMETERS DEPENDING ON PHYSICAL PROPERTIES
      P = (1.022E+05*DENSC*DENSC*SIGMA**3/VISCC**4/DELDEN)**0.15
      DPT = 9.127E-02*SQRT(SIGMA/DELDEN/P)
      AD = 1.445E+04*EXP(0,58*ALOG(DELDEN) - 0.45*ALOG(DENSC) - 0.11*
     1  ALOG(VISCC))
C*** CALCULATE G18 OR PHI, DP, VS, AND VK
   10 RE = 10.75*DI*DI*RPM*DENSC/VISCC
      POM = 1910.*POFUNC(RE)*RPM**3*DI**5/HC/DC**2
      AA = EXP(0.6*ALOG(459.7*SIGMA/DENSC) - 0.4*ALOG(POM))*12.0
      IF(PHI .GT. 1.0) GO TO 12
      VS = VD/PHI + VC/(1.0 - PHI)
      IF(PHI .GE. PHIF) GO TO 18
      VK = VS/(1.0 - PHI)
      VT = VK/CR
      DP = EXP(ALOG(VT/AD)/0.7)
      IF(DP.GT.DPT) DP = DPT
      G18 = DP/AA
      GO TO 20
   12 G18 = PHI - 1.0
      DP = G18*AA
      IF(DP.GT.DPT) GO TO 13
      VT = AD*DP**0.7
      GO TO 14
   13 VT = 1.310E+03*EXP(0,28*ALOG(DELDEN) + 0.10*ALOG(VISCC)
     1     + 0.18*ALOG(SIGMA) - 0.55*ALOG(DENSC))
   14 VK = VT*CR
      IF(VK .LE. VKF) GO TO 18
      PHI = ((VK + VD - VC) - SQRT((VK + VD - VC)**2 - 4.0*VK*VD))/2.0/
     1  VK
      DO 15 I=1,10
      FP = VC*PHI + VD*(1.0 - PHI) - VK*(1.0 - PHI)**2*PHI
      DFDP = VC - VD - VK*(3.0*PHI*PHI - 4.0*PHI + 1.0)
      DELP = FP/DFDP
      IF(ABS(DELP) .LT. 0.00001) GO TO 16
   15 PHI = PHI - DELP
      PRINT 1
   16 PHI = PHI - DELP
      VS = VK*(1.0 - PHI)
      GO TO 20
C*** RDC IS FLOODED BY STRAND CORRELATION
   18 FLOOD = .TRUE.
C*** CALCULATE FLOODING PARAMETERS
   20 AB = (1.0 - 2.0*PHIF)*(1.0 - PHIF)**2
      FFS = VC/VK/AB
      AA = (DELDEN/DENSC)**0.9*(DS/DI)**2.7*(HC/DI)**0.9*(DI/DC)**2.6
      VKL = 1.983E+08*SIGMA*AA/VISCC/DI/RPM**2
      FFL = VC/VKL/AB
      IF(FLOOD) RETURN
C*** CHECK OSCILLATION FACTOR.  IF(OSCFACT .GT. 70.0) HAVE OSCILLATIONS
      OSCFACT = 8419.*DELDEN*DP*DP*P/SIGMA
C*** CALCULATE AXIAL MIXING PARAMETERS
      PEC = COLHT/(0.5 + 0.06*(1.0 - PHI)*DI*RPM*(DS/DC)**2/VC)/HC
      AA = (DI/DC)**2
      AB = AA*((DS/DC)**2 - AA*AA)
      PED = COLHT/(0.5 + 0.45*PHI*DI*RPM*AB/VD)/HC
C*** CALCULATE MASS TRANSFER ESTIMATES
      AA = VD*DENSD/VC/DENSC
      DO 21 I=1,NCOMPS
      NOWSTAG(I) = NOWCIRC(I) = NOWTURB(I) = 0.0
   21 E(I) = AA*KD(I)
      A = 72.0*PHI/DP
      AA = A*COLHT/VC/12.0
      AB = A*COLHT/VD/12.0
      R = COLHT*PHI/VD/12.0
C*** IF MTTYPE .EQ. 0, CALCULATE NOW(I) FOR ALL THREE MODELS
C*** IF MTTYPE .EQ. 1, CALCULATE NOW(I) FOR STAGNANT DROPS AND CALL EETA
      IF(MTTYPE .EQ. 2 .OR. MTTYPE .EQ. 3) GO TO 25
C*** CALCULATIONS FOR STAGNANT DROPS
      DO 22 I=1,NCOMPS
      NWSTAG(I) = 0.001*VS*AA
      NSSTAG(I) = 7.896E-04*DIFFD(I)*AB/DP
   22 NOWSTAG(I) = 1.0/(1.0/NWSTAG(I) + 1.0/E(I)/NSSTAG(I))
      IF(MTTYPE .EQ. 1) GO TO 35
C*** IF MTTYPE .EQ. 2, CALCULATE NOW(I) FOR CIRC DROPS AND CALL EETA
   25 IF(MTTYPE .EQ. 3) GO TO 30
C*** CALCULATIONS FOR CIRCULATING DROPS
      DO 27 I=1,NCOMPS
      NWCIRC(I) = 1.236E-02*SQRT(DIFFC(I)*VS/DP)*AA
      NSCIRC(I) = (7.896E-04*DIFFD(I)/DP + 3.75E-03*VS/
     1  (1.0 + VISCD/VISCC))*AB
   27 NOWCIRC(I) = 1.0/(1.0/NWCIRC(I) + 1.0/E(I)/NSCIRC(I))
      IF(MTTYPE .EQ. 2) GO TO 35
C*** CALCULATIONS FOR TURBULENT DROPS
   30 DO 32 I=1,NCOMPS
      NWTURB(I) = 2.338E-04*POW**0.25*DIFFC(I)**0.66667*
     1  (DENSC/VISCC)**0.41667*AA/ANW
      NSTURB(I) = 7.896E-04*DIFFD(I)*AB/DP/ANS
```

```
32 NOWTURB(I) = 1.0/(1.0/NWTURB(I) + 1.0/E(I)/NSTURB(I))
   IF(MTTYPE .EQ. 0) RETURN
35 DO 36 I=1.NCOMPS
   NOX = NOWSTAG(I) + NOWCIRC(I) + NOWTURB(I)
   EA = E(I)
   CALL EETA(PEC.PED.EA,NOX.ZETA.I.Z.UA.UB)
36 ETA(I) = ZETA
   RETURN
   END RDC
```

FUNCTION POFUNC

```
   FUNCTION POFUNC(RE)
   IF(RE.LT. 5.0E05) GO TO 10
   POFUNC = 0.028
   RETURN
10 IF(RE.GT. 4.0E04) GO TO 15
   POFUNC = 230.54*RE**-0.8
   RETURN
15 IF(RE.GT. 1.5E05) GO TO 20
   POFUNC = 0.93255*RE**-0.28
   RETURN
20 POFUNC = 0.1758*RE**-0.14
   RETURN
   END POFUNC
```

```
        ANALYSIS  OF  RDC  EXTRACTION  RUN  R513          PAGE 1

**** EXPERIMENTAL CONDITIONS
          VELOCITY DISPERSED PHASE =  1.650 FT/HR
          VELOCITY CONTINUOUS PHASE = 13.045 FT/HR
          TEMPERATURE = 21.0 DEGREES C
          ROTATIONAL SPEED =  800.0 RPM
          HOLD-UP = .012352      (CALCULATED)
          DIA =   .2000           (ESTIMATED)


**** COLUMN DIMENSIONS
          DISC DIAMETER =  1.50 INCH
          STATOR HOLE DIAMETER =  2.25 INCH
          COLUMN DIAMETER =  3.00 INCH
          COMPARTMENT HEIGHT =  1.00 INCH
          COLUMN HEIGHT =  29.190 INCH


**** PHYSICAL PROPERTIES
          DENSITY DISPERSED PHASE =  .87920 GRAM/CC
          DENSITY CONTINUOUS PHASE =  .99790 GRAM/CC
          INTERFACIAL TENSION =  13.990 DYNE/CM
          VISCOSITY DISPERSED PHASE =   .7080 CP
          VISCOSITY CONTINUOUS PHASE =   .9642 CP


**** FLOODING CHARACTERISTICS
          VD/VC =  .12645
          PHI FLOODING = .181542
          VK (LOGSDAIL) =  127.52 FT/HR
          FRACTION OF FLOODING (L) = .2398
          VK (STRAND) =  140.63 FT/HR
          FRACTION OF FLOODING (S) = .2058
          DROP DIAMETER = .021324 INCH
          TRANSITION DROP DIA = .173053 INCH
          POWER PER MASS =  164.72 FT-LBF/HR-LBM
          OSCILLATION FACTOR =   .8485


**** AXIAL MIXING CHARACTERISTICS
          PED =  29.0357
          PEC =   8.1671
        ANALYSIS  OF  RDC  EXTRACTION  RUN  R513          PAGE 2

**** SOLUTE DIFFUSIVITIES, DISTRIBUTION COEFFICIENTS, AND E(I)
                 10**5 * SQFT/HR
   SOLUTE       DD(I)       DC(I)              KD(I)          E(I)

  ME ACE         6.45        3.93               3.64           .41
  ET ACE         5.97        3.40              11.20          1.25
  I-PR ACE       5.60        3.04              34.10          3.80
  O-CRESOL       5.57        3.02             206.00         22.95

**** MASS TRANSFER ESTIMATES
          A =  41.71 SQFT/CUFT
          RISE TIME =  1.821E-02 HR

 ** STAGNANT DROPS
   SOLUTE              NW          NS          NOW

  ME ACE              1.141      14.686        .958
  ET ACE              1.141      13.593       1.069
  I-PR ACE            1.141      12.750       1.115
  O-CRESOL            1.141      12.682       1.137

 ** CIRCULATING DROPS
   SOLUTE              NW          NS          NOW

  ME ACE             15.806      34.292       7.387
  ET ACE             14.702      33.109      10.843
  I-PR ACE           13.902      32.267      12.486
  O-CRESOL    -      13.656      32.198      13.601

 ** TURBULENT DROPS
   SOLUTE              NW          NS          NOW

  ME ACE              2.352      14.686       1.686
  ET ACE              2.136      13.593       1.897
  I-PR ACE            1.902      12.750       1.904
  O-CRESOL            1.974      12.682       1.960

**** EXPERIMENTAL REMOVALS
   SOLUTE     FEED PPM     PROD PPM         ETA

  ME ACE        227.0        181.0        .79736
  ET ACE        270.0         81.6        .30222
  I-PR ACE      675.0         85.3        .12618
  O-CRESOL     5622.0        255.0        .04536
```

```
              ANALYSIS OF DATA FOR EXTRACTION RUN NUMBER  RS13

         PEX =   8.1871      PEY =  29.0357                       4 COMPONENTS

**** FOR ME ACE     E =     .4100 AND ZETA = .79736 GIVING NOX =     .337

*PROFILE Z(0.0)   Z(0.1)   Z(0.2)   Z(0.3)   Z(0.5)   Z(0.7)   Z(0.8)   Z(0.9)   Z(1.0)
 MIXED   .97933   .96208   .94407   .92526   .88524   .84301   .82259   .80544   .79736
 PLUG   1.00000   .98363   .96659   .94957   .91016   .86910   .84558   .82202   .79736

*SENSITIVITY -- DX = CHANGE IN NOX CAUSED BY A 1 PERCENT DECREASE IN X
    DZETA =  2.26E-02 , DE =  1.75E-03 , DPEX =  1.20E-04 , DPEY =  8.98E-05

**** FOR ET ACE     E =    1.2500 AND ZETA = .30222 GIVING NOX =    2.520

*PROFILE Z(0.0)   Z(0.1)   Z(0.2)   Z(0.3)   Z(0.5)   Z(0.7)   Z(0.8)   Z(0.9)   Z(1.0)
 MIXED   .96333   .82640   .75250   .63148   .54711   .42404   .36901   .32374   .30222
 PLUG   1.00000   .91771   .83849   .76222   .61913   .48451   .42143   .36069   .30222

*SENSITIVITY -- DX = CHANGE IN NOX CAUSED BY A 1 PERCENT DECREASE IN X
    DZETA =  3.49E-02 , DE =  2.53E-02 , DPEX =  5.58E-03 , DPEY =  1.67E-03

**** FOR I-PR ACE  E =    3.8000 AND ZETA = .12618 GIVING NOX =    3.249

*PROFILE Z(0.0)   Z(0.1)   Z(0.2)   Z(0.3)   Z(0.5)   Z(0.7)   Z(0.8)   Z(0.9)   Z(1.0)
 MIXED   .81365   .67452   .55819   .46068   .31050   .20570   .16715   .13868   .12617
 PLUG   1.00000   .82708   .68278   .56235   .37797   .24956   .20081   .16013   .12618

*SENSITIVITY -- DX = CHANGE IN NOX CAUSED BY A 1 PERCENT DECREASE IN X
    DZETA =  2.21E-02 , DE =  4.45E-03 , DPEX =  6.94E-03 , DPEY =  8.30E-04

**** FOR O-CRESOL  E =  22.9500 AND ZETA = .04535 GIVING NOX =    4.339

*PROFILE Z(0.0)   Z(0.1)   Z(0.2)   Z(0.3)   Z(0.5)   Z(0.7)   Z(0.8)   Z(0.9)   Z(1.0)
 MIXED   .73268   .54352   .43327   .29935   .16413   .08995   .06706   .05169   .04536
 PLUG   1.00000   .73655   .54234   .39920   .21593   .11637   .08523   .06228   .04536

*SENSITIVITY -- DX = CHANGE IN NOX CAUSED BY A 1 PERCENT DECREASE IN X
    DZETA =  1.84E-02 , DE =  2.24E-03 , DPEX =  1.05E-02 , DPEY =  3.12E-04
```

List of Experimental Data.

In the Table H to follow, the experimental data for runs conducted in the RDC extractor are listed. The table entries include the measured phase velocities, the column temperature, the dimensions of the column and its internals, the disc rotational speed, and the feed and product aqueous-phase concentrations. F_s/F_w is the ratio of solvent mass flow rate to water mass flow rate; when this quantity is multiplied by K_d, the extraction factor, E, for each solute results. Also included in the table are the estimates of physical properties and the following quantities calculated in the computer program:

G_{18} = value assumed to give correct drop size

ϕ_{calc} = calculated solvent hold-up

ϕ_{meas} = measured solvent hold-up

d_p = average drop diameter

a = interfacial area per column volume

Pe_c = water-phase Peclet number

Pe_d = solvent-phase Peclet number

FF = percentage of flooding according to Logsdail, et al. (1957)

POM = power per unit mass

Table H. RDC Extractor Data

RDC extractor run # RS1A Temperature = 22.0°C

Dispersed phase = Isobutylene

Continuous phase = Prepared Waste Water

V_d = 3.704 ft/hr, V_c = 6.210 ft/hr, F_s/F_w = 0.3538

d_i = 1.50 inch, d_s = 2.25 inch, H = 23.00 inch

ρ_d = 0.5917 gm/cc, μ_d = 0.181 cp, N = 1430.0 RPM

ρ_c = 0.9978 gm/cc, μ_c = 0.955 cp, σ = 41.6 dyne/cm

G_{18} = 0.337, ϕ_{calc} = 0.0078, ϕ_{meas} = --

d_p = 0.0417 inch, a = 13.43 ft^2/ft^3, Pe_d = 30.52

FF = 8.3%, POM = 586.6 ft-lb_f/hr-lb_m, Pe_c = 1.906

Solute	D_d	D_c	K_d	Feed Water (ppm)	Product Water (ppm)	% Removal
	$(10^5$	$ft^2/hr)$				
1. MEK	24.1	3.65	2.49	2109	639	69.7
2. DEK	22.5	3.22	13.4	4297	183	95.7
3. n-BuAc	20.6	2.76	168.	4393	77.3	98.2

RDC extractor run # RS1B Temperature = 22.0°C

Dispersed phase = Isobutylene

Continuous phase = Prepared Waste Water

V_d = 1.226 ft/hr, V_c = 6.210 ft/hr, F_s/F_w = 0.1171

d_i = 1.50 inch, d_s = 2.25 inch, H = 23.00 inch

ρ_d = 0.5917 gm/cc, μ_d = 0.181 cp, N = 1430.0 RPM

ρ_c = 0.9978 gm/cc, μ_c = 0.955 cp, σ = 41.6 dyne/cm

G_{18} = 0.337, ϕ_{calc} = 0.0026, ϕ_{meas} = --

d_p = 0.0417 inch, a = 4.42 ft^2/ft^3, Pe_d = 30.58

FF = 4.8%, POM = 586.6 ft-lb_f/hr-lb_m, Pe_c = 1.897

Solute	D_d	D_c	K_d	Feed Water (ppm)	Product Water (ppm)	% Removal
	$(10^5$	$ft^2/hr)$				
1. MEK	24.1	3.65	2.49	2109	1340	36.5
2. DEK	22.5	3.22	13.4	4297	888	79.3
3. n-BuAc	20.6	2.76	168.	4393	288	93.4

Table H. RDC Extractor Data (Continued)

RDC extractor run # RS2 Temperature = 22.0°C

Dispersed phase = n-Butyl Acetate

Continuous phase = Prepared Waste Water

V_d = 1.909 ft/hr, V_c = 14.054 ft/hr, F_s/F_w = 0.1196

d_i = 1.50 inch, d_s = 2.25 inch, H = 23.00 inch

ρ_d = 0.8788 gm/cc, μ_d = 0.704 cp, N = 617.0 RPM

ρ_c = 0.9978 gm/cc, μ_c = 0.955 cp, σ = 13.9 dyne/cm

G_{18} = 0.200, ϕ_{calc} = 0.0120, ϕ_{meas} = --

d_p = 0.0269 inch, a = 32.17 ft^2/ft^3, Pe_d = 27.79

FF = 15.6%, POM = 92.3 ft-lb$_f$/hr-lb$_m$, Pe_c = 8.530

Solute	D_d (10^5	D_c ft^2/hr)	K_d	Feed Water (ppm)	Product Water (ppm)	% Removal
1. MEK	6.21	3.65	4.56	2213	1413	36.2
2. DEK	5.79	3.22	16.2	4314	1485	65.6
3. Phenol	6.04	3.47	57.0	6143	1073	82.5

Comment: Product water concentrations calculated by material balance from loaded solvent analysis.

Table H. RDC Extractor Data (Continued)

RDC extractor run # RS3 Temperature = 22.0°C

Dispersed phase = n-Butyl Acetate

Continuous phase = Prepared Waste Water

V_d = 1.705 ft/hr, V_c = 15.388 ft/hr, F_s/F_w = 0.0974

d_i = 1.50 inch, d_s = 2.25 inch, H = 29.75 inch

ρ_d = 0.8788 gm/cc, μ_d = 0.704 cp, N = 805.0 RPM

ρ_c = 0.9978 gm/cc, μ_c = 0.955 cp, σ = 13.9 dyne/cm

G_{18} = 0.200, ϕ_{calc} = 0.0130, ϕ_{meas} = 0.0630

d_p = 0.0213 inch, a = 43.97 ft^2/ft^3, Pe_d = 29.24

FF = 17.3%, POM = 165.7 $ft\text{-}lb_f/hr\text{-}lb_m$, Pe_c = 9.554

	D_d	D_c	K_d	Feed Water	Product Water	%
Solute	(10^5	ft^2/hr)		(ppm)	(ppm)	Removal
1. Acetone	6.77	4.30	1.05	38.0	34.3	9.7
2. MEK	6.21	3.65	4.56	217	126	41.9
3. Benzene	6.21	3.65	61.5	169	30.5	82.0
4. Phenol	6.04	3.47	57.0	13300	308	97.7
5. o-Cresol	5.61	3.05	206.	2107	25.4	98.8

Table H. RDC Extractor Data (Continued)

RDC extractor run # RS4 Temperature = 26.8°C

Dispersed phase = Isobutylene

Continuous phase = Prepared Waste Water

V_d = 2.152 ft/hr, V_c = 12.622 ft/hr, F_s/F_w = 0.0996

d_i = 1.75 inch, d_s = 2.00 inch, H = 28.31 inch

ρ_d = 0.5856 gm/cc, μ_d = 0.175 cp, N = 1430.0 RPM

ρ_c = 0.9966 gm/cc, μ_c = 0.855 cp, σ = 40.6 dyne/cm

G_{18} = 0.337, ϕ_{calc} = 0.00658, ϕ_{meas} = 0.00658

d_p = 0.0324 inch, a = 14.64 ft^2/ft^3, Pe_d = 31.99

FF = 13.8%, POM = 1070.1 ft-lb_f/hr-lb_m, Pe_c = 4.922

Solute	D_d (10^5	D_c ft^2/hr)	K_d	Feed Water (ppm)	Product Water (ppm)	% Removal
1. Acetone	27.7	4.88	0.63	29.9	28.2	5.7
2. MEK	25.4	4.14	2.49	124	83.3	22.8
3. Benzene	25.4	4.15	407.	68.5	60.4	11.8
4. n-BuAc	21.6	3.13	168.	5457	10.8	99.8
5. Phenol	24.7	3.94	0.70	605	522	13.7
6. o-Cresol	22.9	3.46	4.80	72.8	17.0	76.6

Comment: Feed water is the product water from run RS3.

Table H. RDC Extractor Data (Continued)

RDC extractor run # RS6A Temperature = 24.2°C

Dispersed phase = n-Butyl Acetate

Continuous phase = Lube Oil Refining Waste Water

V_d = 1.005 ft/hr, V_c = 8.743 ft/hr, F_s/F_w = 0.1010

d_i = 1.50 inch, d_s = 2.25 inch, H = 29.00 inch

ρ_d = 0.8765 gm/cc, μ_d = 0.687 cp, N = 1100.0 RPM

ρ_c = 0.9972 gm/cc, μ_c = 0.907 cp, σ = 13.5 dyne/cm

G_{18} = 0.200, ϕ_{calc} = 0.0088, ϕ_{meas} = --

d_p = 0.0161 inch, a = 39.14 ft^2/ft^3, Pe_d = 22.13

FF = 28.0%, POM = 316.2 ft-lb_f/hr-lb_m, Pe_c = 4.256

	D_d	D_c	K_d	Feed Water	Product Water	% Removal
Solute	(10^5	ft^2/hr)		(ppm)	(ppm)	
1. MEK	6.41	3.87	4.56	12216	5883	51.8
2. Phenol	6.23	3.69	57.0	8751	104	98.8
3. O-Cresol	5.79	3.24	206.	892	6.5	99.3

RDC extractor run # RS6B Temperature = 23.4°C

Dispersed phase = n-Butyl Acetate

Continuous phase = Lube Oil Refining Waste Water

V_d = 3.023 ft/hr, V_c = 8.743 ft/hr, F_s/F_w = 0.3042

d_i = 1.50 inch, d_s = 2.25 inch, H = 29.19 inch

ρ_d = 0.8774 gm/cc, μ_d = 0.690 cp, N = 1100.0 RPM

ρ_c = 0.9974 gm/cc, μ_c = 0.932 cp, σ = 13.7 dyne/cm

G_{18} = 0.200, ϕ_{calc} = 0.0272, ϕ_{meas} = 0.00214

d_p = 0.0162 inch, a = 121.1 ft^2/ft^3, Pe_d = 21.88

FF = 45.6%, POM = 323.0 ft-lb_f/hr-lb_m, Pe_c = 4.359

	D_d	D_c	K_d	Feed Water	Product Water	% Removal
Solute	(10^5	ft^2/hr)		(ppm)	(ppm)	
1. MEK	6.36	3.76	4.56	12216	2452	82.3
2. Phenol	6.19	3.58	57.0	8751	77.0	99.1
3. o-Cresol	5.75	3.14	206.	892	4.3	99.5

Table H. RDC Extractor Data (Continued)

RDC extractor run # RS7A Temperature = 23.3°C

Dispersed phase = Isobutylene

Continuous phase = Treated Lube Oil Refining Waste Water

V_d = 1.506 ft/hr, V_c = 8.743 ft/hr, F_s/F_w = 0.1019

d_i = 1.75 inch, d_s = 2.00 inch, H = 29.31 inch

ρ_d = 0.5900 gm/cc, μ_d = 0.179 cp, N = 1450.0 RPM

ρ_c = 0.9975 gm/cc, μ_c = 0.926 cp, σ = 41.3 dyne/cm

G_{18} = 0.337, ϕ_{calc} = 0.0047, ϕ_{meas} = 0.0362

d_p = 0.0319 inch, a = 10.51 ft^2/ft^3, Pe_d = 32.76

FF = 10.6%, POM = 1136.1 $ft\text{-}lb_f/hr\text{-}lb_m$, Pe_c = 3.573

Solute	D_d $(10^5$	D_c $ft^2/hr)$	K_d	Feed Water (ppm)	Product Water (ppm)	% Removal
1. MEK	24.5	3.78	2.49	5573	3597	35.5
2. n-BuAc	20.9	2.86	168.	7133	11.0	99.8
3. Phenol	23.8	3.60	0.70	306	227	25.8
4. o-Cresol	22.2	3.16	4.80	24.2	2.3	90.5

Comment: Feed water is the product water from run RS6A.

Table H. RDC Extractor Data (Continued)

RDC extractor run # RS7B Temperature = 23.3°C

Dispersed phase = Isobutylene

Continuous phase = Treated Lube Oil Refining Waste Water

V_d = 1.506 ft/hr, V_c = 8.743 ft/hr, F_s/F_w = 0.1019

d_i = 1.75 inch, d_s = 2.00 inch, H = 28.88 inch

ρ_d = 0.5900 gm/cc, μ_d = 0.179 cp, N = 1450.0 RPM

ρ_c = 0.9975 gm/cc, μ_c = 0.926 cp, σ = 41.3 dyne/cm

G_{18} = 0.337, ϕ_{calc} = 0.0047, ϕ_{meas} = 0.0346

d_p = 0.0319 inch, a = 10.51 ft^2/ft^3, Pe_d = 32.28

FF = 10.6%, POM = 1136.1 $ft\text{-}lb_f/hr\text{-}lb_m$, Pe_c = 3.521

Solute	D_d (10^5	D_c ft^2/hr)	K_d	Feed Water (ppm)	Product Water (ppm)	% Removal
1. MEK	24.5	3.78	2.49	2801	1891	32.5
2. n-BuAc	20.9	2.86	168.	6791	15.2	99.8
3. Phenol	23.8	3.60	0.70	229	190	17.0
4. o-Cresol	22.2	3.16	4.80	18.0	2.8	84.4

Comment: Feed water is the product water from run RS6B.

Table H. RDC Extractor Data (Continued)

RDC extractor run # RS8 Temperature = 21.2°C

Dispersed phase = 48.7% n-Butyl Acetate in Isobutylene

Continuous phase = Lube Oil Refining Waste Water

V_d = 3.072 ft/hr, V_c = 11.003 ft/hr, F_s/F_w = 0.2049

d_i = 1.50 inch, d_s = 2.00 inch, H = 29.00 inch

ρ_d = 0.7325 gm/cc, μ_d = 0.279 cp, N = 1090.0 RPM

ρ_c = 0.9979 gm/cc, μ_c = 0.973 cp, σ = 33.1 dyne/cm

G_{18} = 0.171, ϕ_{calc} = 0.0157, ϕ_{meas} = --

d_p = 0.0233 inch, a = 48.47 ft^2/ft^3, Pe_d = 33.77

FF = 14.1%, POM = 327.8 $ft\text{-}lb_f/hr\text{-}lb_m$, Pe_c = 6.590

Solute	D_d	D_c	K_d	Feed Water (ppm)	Product Water (ppm)	% Removal
	(10^5	ft^2/hr)				
1. Acetone	17.0	4.20	0.83	24.6	12.1	50.8
2. MEK	15.6	3.57	3.50	108	54.9	49.2
3. Phenol	15.2	3.40	28.1	17170	1902	88.9
4. o-Cresol	14.1	2.99	100.	2660	124	95.3
5. Benzene	15.6	3.57	239.	36.9	9.2	75.1

RDC extractor run # RS9 Temperature = 22.3°C

Dispersed phase = 53.1% n-Butyl Acetate in Isobutylene

Continuous phase = Prepared Waste Water

V_d = 3.715 ft/hr, V_c = 12.692 ft/hr, F_s/F_w = 0.2182

d_i = 1.75 inch, d_s = 2.00 inch, H = 28.88 inch

ρ_d = 0.7438 gm/cc, μ_d = 0.292 cp, N = 1090.0 RPM

ρ_c = 0.9977 gm/cc, μ_c = 0.948 cp, σ = 31.7 dyne/cm

G_{18} = 0.171, ϕ_{calc} = 0.0238, ϕ_{meas} = 0.0238

d_p = 0.0186 inch, a = 92.31 ft^2/ft^3, Pe_d = 25.90

FF = 22.5%, POM = 542.2 $ft\text{-}lb_f/hr\text{-}lb_m$, Pe_c = 6.544

Solute	D_d	D_c	K_d	Feed Water (ppm)	Product Water (ppm)	% Removal
	(10^5	ft^2/hr)				
1. MEK	15.0	3.68	3.59	424	91.3	75.5
2. Phenol	14.6	3.50	30.6	17320	93.4	99.5

Table H. RDC Extractor Data (Continued)

RDC extractor run # RS10 Temperature = 20.8°C

Dispersed phase = Isobutylene

Continuous phase = Ethylene Quench Waste Water

V_d = 2.141 ft/hr, V_c = 12.583 ft/hr, F_s/F_w = 0.1010

d_i = 1.75 inch, d_s = 2.00 inch, H = 28.81 inch

ρ_d = 0.5923 gm/cc, μ_d = 0.183 cp, N = 1450.0 RPM

ρ_c = 0.9980 gm/cc, μ_c = 0.983 cp, σ = 41.8 dyne/cm

G_{18} = 0.220, ϕ_{calc} = 0.0093, ϕ_{meas} = 0.0217

d_p = 0.0208 inch, a = 32.10 ft^2/ft^3, Pe_d = 27.33

FF = 16.0%, POM = 1154.9 ft-lb_f/hr-lb_m, Pe_c = 4.944

Solute	D_d	D_c	K_d	Feed Water (ppm)	Product Water (ppm)	% Removal
	(10^5	ft^2/hr)				
1. Benzene	23.8	3.54	407.	71.1	2.9	95.9
2. Toluene	22.2	3.12	1690.	40.5	2.3	94.3
3. Xylenes	21.1	2.83	--	40.3	<1	>97
4. Phenol	23.1	3.36	0.70	66.9	63.1	5.7

Comment: Feed COD = 1880 ppm; Product COD = 1209 ppm.

Table H. RDC Extractor Data (Continued)

RDC extractor run # RS11 Temperature = 23.4°C

Dispersed phase = Isobutane

Continuous phase = Ethylene Quench Waste Water

V_d = 2.198 ft/hr, V_c = 12.528 ft/hr, F_s/F_w = 0.0973

d_i = 1.75 inch, d_s = 2.00 inch, H = 29.50 inch

ρ_d = 0.5530 gm/cc, μ_d = 0.201 cp, N = 1450.0 RPM

ρ_c = 0.9974 gm/cc, μ_c = 0.924 cp, σ = 47.7 dyne/cm

G_{18} = 0.200, ϕ_{calc} = 0.0090, ϕ_{meas} = 0.0096

d_p = 0.0207 inch, a = 31.41 ft^2/ft^3, Pe_d = 28.83

FF = 12.3%, POM = 1135.4 $ft\text{-}lb_f/hr\text{-}lb_m$, Pe_c = 5.041

Solute	D_d (10^5	D_c ft^2/hr)	K_d	Feed Water (ppm)	Product Water (ppm)	% Removal
1. Benzene	21.9	3.79	338.	81.2	2.4	97.0
2. Toluene	20.4	3.35	1460.	43.8	1.6	96.3
3. Xylenes	19.3	3.03	--	33.6	<1	>97
4. Phenol	21.2	3.58	0.20	68.2	66.0	3.2

Comment: Feed COD = 1880 ppm; Product COD = 699 ppm.
Turbidity reduced by 72%.

Table H. RDC Extractor Data (Continued)

RDC extractor run # RS12 Temperature = 22.2°C

Dispersed phase = 2-Ethyl Hexanol

Continuous phase = Neutralized Oxychlorination Waste Water

V_d = 1.501 ft/hr, V_c = 11.766 ft/hr, F_s/F_w = 0.1063

d_i = 1.50 inch, d_s = 2.25 inch, H = 30.00 inch

ρ_d = 0.8311 gm/cc, μ_d = 8.038 cp, N = 800.0 RPM

ρ_c = 0.9977 gm/cc, μ_c = 0.964 cp, σ = 8.5 dyne/cm

G_{18} = 0.200, ϕ_{calc} = 0.0112, ϕ_{meas} = 0.0156

d_p = 0.0159 inch, a = 50.94 ft^2/ft^3, Pe_d = 29.85

FF = 26.1%, POM = 164.7 $ft\text{-}lb_f/hr\text{-}lb_m$, Pe_c = 7.686

Solute	D_d	D_c	K_d	Feed Water (ppm)	Product Water (ppm)	% Removal
	(10^5	ft^2/hr)				
1. Ethanol	0.64	4.99	1.0	286	265	7.3
2. EDC	0.55	3.73	200.	1505	20	98.7
3. ECH	0.58	4.11	5.0	1636	1292	21.0
4. Chloral Hyd.	0.49	3.08	140.	15220	7726	49.2

Comment: Water phase contained 9.26 wt. % NaCl.

Table H. RDC Extractor Data (Continued)

RDC extractor run # RS13 Temperature = 21.6°C

Dispersed phase = n-Butyl Acetate

Continuous phase = Prepared Waste Water

V_d = 1.650 ft/hr, V_c = 13.049 ft/hr, F_s/F_w = 0.1114

d_i = 1.50 inch, d_s = 2.25 inch, H = 29.19 inch

ρ_d = 0.8792 gm/cc, μ_d = 0.708 cp, N = 800.0 RPM

ρ_c = 0.9979 gm/cc, μ_c = 0.964 cp, σ = 13.9 dyne/cm

$G_{1º}$ = 0.200, ϕ_{calc} = 0.0124, ϕ_{meas} = 0.0428

d_p = 0.0213 inch, a = 41.71 ft^2/ft^3, Pe_d = 29.04

FF = 24.0%, POM = 164.7 $ft\text{-}lb_f/hr\text{-}lb_m$, Pe_c = 8.187

	D_d	D_c	K_d	Feed Water	Product Water	% Removal
Solute	$(10^5$	$ft^2/hr)$		(ppm)	(ppm)	
1. MeAc	6.45	3.93	3.64	227	181	20.3
2. EtAc	5.97	3.40	11.2	270	81.6	69.8
3. i-PrAc	5.60	3.04	34.1	676	85.3	87.4
4. o-Cresol	5.57	3.02	206.	5622	255.	95.5

Table H. RDC Extractor Data (Continued)

RDC extractor run # RS14 Temperature = 25.3°C

Dispersed phase = Isobutylene

Continuous phase = Prepared Waste Water

V_d = 9.986 ft/hr, V_c = 8.607 ft/hr, F_s/F_w = 0.6867

d_i = 1.75 inch, d_s = 2.00 inch, H = 29.00 inch

ρ_d = 0.5869 gm/cc, μ_d = 0.177 cp, N = 1200 RPM

ρ_c = 0.9970 gm/cc, μ_c = 0.883 cp, σ = 40.9 dyne/cm

G_{18} = 0.337, ϕ_{calc} = 0.0270

d_p = 0.0392 inch, a = 49.62 ft^2/ft^3, Pe_d = 36.90

FF = 19.4%, POM = 670.08 ft-lb$_f$/hr-lb$_m$, Pe_c = 4.246

	D_d	D_c	K_d	Feed Water	Product Water	% Removal
Solute	(10^5	ft^2/hr)		(ppm)	(ppm)	
Crotonaldehyde	25.35	3.34	2.48	5572	936	83.2

RDC extractor run # RS15 Temperature = 22.7 °C

Dispersed phase = 48.2% n-Butyl Acetate in Isobutylene

Continuous phase = Phenolic Resin Plant Water

V_d = 1.844 ft/hr, V_c = 6.583 ft/hr, F_s/F_w = 0.2059

d_i = 1.75 inch, d_s = 2.00 inch, H = 28.18 inch

ρ_d = 0.7294 gm/cc, μ_d = 0.285 cp, N = 1200 RPM

ρ_c = 0.9976 gm/cc, μ_c = 0.940 cp, σ = 32.1 dyne/cm

G_{18} = 0.0171 , ϕ_{calc} = 0.0115,

d_p = 0.0171 inch, a = 48.56 ft^2/ft^3, Pe_d = 24.30

FF = 12.9 %, POM = 681.8 ft-lb$_f$/hr-lb$_m$, Pe_c = 3.163

	D_d	D_c	K_d	Feed Water	Product Water	% Removal
Solute	(10^5	ft^2/hr)		(ppm)	(ppm)	
Methanol	14.18	4.68	0.10	12000	11510	4.1
Formaldehyde	17.12	7.36	0.15	17370	16450	5.3
Phenol	6.12	3.53	6.15	48270	483	99.0

Table H. RDC Extractor Data (Continued)

RDC extractor run # RS16 Temperature = 23.4 °C
Dispersed phase = n-Butyl Acetate
Continuous phase = Phenolic Resin Plant Water
V_d = 0.804 ft/hr, V_c = 5.936 ft/hr, F_s/F_w = 0.1188
d_i = 1.50 inch, d_s = 2.25 inch, H = 30.50 inch
ρ_d = 0.8744 gm/cc, μ_d = 0.690 cp, N = 1250 RPM
ρ_c = 0.9974 gm/cc, μ_c = 0.932 cp, σ = 13.7 dyne/cm
G_{18} = 0.200 , ϕ_{calc} = 0.0075
d_p = 0.0144 inch, a = 37.34 ft^2/ft^3, Pe_d = 20.58
FF = 26.5 %, POM = 428.1 ft-lb_f/hr-lb_m, Pe_c = 2.753

Solute	D_d (10^5	D_c ft^2/hr)	K_d	Feed Water (ppm)	Product Water (ppm)	% Removal
Methanol	14.31	4.69	0.10	12000	7608	36.6
Formaldehyde	17.30	7.44	0.15	17370	10370	40.3
Phenol	6.19	3.58	12.0	48270	6082	87.4

RDC extractor run # RS17 Temperature = 24.5 °C
Dispersed phase = Methyl Isobutyl Ketone
Continuous phase = Hydrofiner Waste Water
V_d = 1.682 ft/hr, V_c = 10.717 ft/hr, F_s/F_w = 0.1249
d_i = 1.50 inch, d_s = 2.25 inch, H = 30.25 inch
ρ_d = 0.7914 gm/cc, μ_d = 0.542 cp, N = 1250 RPM
ρ_c = 0.9972 gm/cc, μ_c = 0.898 cp, σ = 9.90 dyne/cm
G_{18} = 0.200 , ϕ_{calc} = 0.0134
d_p = 0.0120 inch, a = 80.42 ft^2/ft^3, Pe_d = 22.55
FF = 41.6%, POM = 415.6 ft-lb_f/hr-lb_m, Pe_c = 4.782

Solute	D_d (10^5	D_c ft^2/hr)	K_d	Feed Water (ppm)	Product Water (ppm)	% Removal
Phenol	6.24	3.74	68.0	400	< 1	> 99.8

Comment: Feed COD = 17530 ppm
MIBK Concentration in Product Water = 15680 ppm
(COD 42500 ppm)

Table H. RDC Extractor Data (Continued)

RDC extractor run #RS18 Temperature = 24.2 °C

Dispersed phase = 49.5% Methyl Isobutyl Ketone in Isobutylene

Continuous phase = Hydrofiner Waste Water

V_d = 2.052 ft/hr, V_c = 6.808 ft/hr, F_s/F_w = 0.2091

d_i = 1.75 inch, d_s = 2.00 inch, H = 30.38 inch

ρ_d = 0.7916 gm/cc, μ_d = 0.265 cp, N = 1150 RPM

ρ_c = 0.9972 gm/cc, μ_c = 0.907 cp, σ = 29.7 dyne/cm

G_{18} = 0.171 , ϕ_{calc} = 0.0150

d_p = 0.0171 inch, a = 63.14 ft^2/ft^3, Pe_d = 24.47

FF = 16.8%, POM = 601.3 ft-lb_f/hr-lb_m, Pe_c = 3.676

Solute	D_d (10^5	D_c ft^2/hr)	K_d	Feed Water (ppm)	Product Water (ppm)	% Removal
Phenol	6.23	3.69	34.0	400	< 1	> 99

Comment: Feed COD = 17530 ppm; Product COD = 18580 ppm
MIBK Concentration in Product Water = 3150 ppm
(COD 9000 ppm)

RDC extractor run #RS19 Temperature = 21.8°C

Dispersed phase = Isobutylene

Continuous phase = Styrene Waste Water

V_d = 1.480 ft/hr, V_c = 8.170 ft/hr, F_s/F_w = 0.1072

d_i = 1.75 inch, d_s = 2.00 inch, H = 30.00 inch

ρ_d = 0.5926 gm/cc, μ_d = 0.181 cp, N = 1250 RPM

ρ_c = 0.9978 gm/cc, μ_c = 0.959 cp, σ = 41.7 dyne/cm

G_{18} = 0.337, ϕ_{calc} = 0.0043

d_p = 0.0376 inch, a = 8.27 ft^2/ft^3, Pe_d = 36.06

FF = 7.93%, POM = 766.11 ft-lb_f/hr-lb_m, Pe_c = 3.811

Solute	D_d (10^5	D_c ft^2/hr)	K_d	Feed Water (ppm)	Product Water (ppm)	% Removal
1. Benzene	24.00	3.62	407.	290	10	96.6
2. Ethylbenzene	25.17	2.90		120	4	96.7
3. Styrene	26.19	2.99		15	<1	>93

APPENDIX I

LABORATORY EXTRACTIONS OF OXYCHLORINATION WASTE WATER

One of the samples of industrial waste water which was studied in this work came from an oxychlorination plant. The most serious pollutant present in this waste water was found to be chloral hydrate, which was present at a concentration of about 1.5 weight %. This waste water also contained between 1.5 and 5.8 weight % HCl, between 1500 and 3460 ppm ethylene dichloride, and less than 500 ppm of several other organic compounds.

The measurement of the equilibrium distribution coefficient for chloral hydrate distributing between salt-free water and 2-ethyl hexanol indicated that this was an excellent solvent. K_d varied from 50 with 500 ppm in the aqueous phase to 17 with 15,000 ppm in the aqueous phase. However, when a sample of neutralized oxychlorination waste water was contacted at a low flow ratio with 2-ethyl hexanol in the RDC extractor (Run RS12), the removal efficiency was found to be only 49% rather than about 98% expected for a solute with such a large value of K_d. In this appendix several experiments are discussed which show that this low removal is probably due to a slow chemical reaction which accompanies the transfer of chloral from the water phase to the solvent phase.

Initial Experiment.

An aqueous solution containing ethyl acetate, n-butyl acetate, and chloral hydrate was prepared. An accurately measured quantity (359 gm) of this solution was added to a 500-ml separatory funnel. A 50-gm sample of 2-ethyl hexanol was added, and shaking of the mixture was begun immediately. After a precisely measured time interval, about 30 ml of the dispersion was removed into a 60 ml separatory funnel, and shaking of the 500-ml separatory was continued. After 40 seconds to allow the phases to separate in the 60-ml separatory funnel, about 10 ml of aqueous phase was drained into a sample bottle. Three samples were collected from three 60-ml separatory funnels before the shaking of the 500-ml separatory funnel was terminated. These samples were analyzed for the three solutes using the gas chromatograph, and then the contents of each 60-ml separatory funnel and of each sample bottle (only a few microliters were used for the GC analysis) were added back into the 500-ml separatory funnel. After 24 hours with occasional shaking, the aqueous phase from the equilibrated mixture was analyzed using the GC.

Results and Discussion on Initial Experiment.

In Table I1 the results are shown from the analyses of the initial aqueous phase, of the unequilibrated samples taken at 1, 4, and 10 minutes after shaking began, and of the sample taken after 24 hours which is assumed to be at equilibrium.

Table Il. Results from Extraction of a Prepared Water Solution using 2-Ethyl Hexanol

Initially pure solvent added to 500-ml separatory funnel = 50.0 grams

Prepared water solution added to 500-ml separatory funnel = 359. grams

Water phase analyses (concentrations in ppm by weight):

Time after beginning to shake funnel (min)	Ethyl Acetate	n-Butyl Acetate	Chloral Hydrate
Initial	1,802	4,410	15,000
1	896	264	10,350
4	883	262	8,750
10	809	235	5,220
∞	860	244	2,360

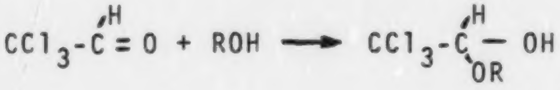
Apparent values of K_d:

1	7.26	113	3.2
4	7.47	114	5.1
10	8.81	128	13.5
∞	7.85	123	38.5

It appears that both ethyl acetate and n-butyl acetate had essentially equilibrated within the first minute of shaking. However, even after 10 minutes of shaking, the concentration of chloral hydrate is still changing with time.

Another way of presenting the results is to calculate an apparent value of K_d based on a material balance. From the known quantities of the two phases, K_d can be calculated from the initial and final concentrations by assuming equilibrium is achieved. These results shown at the bottom of Table II again indicate a slow approach to equilibrium in the case of chloral hydrate. The final value of K_d for chloral hydrate after a long time (24 hours) agreed well with the separately determined equilibrium measurements of 38.

A possible explanation for the observed slow rate of mass transfer for chloral can be postulated based on the extensive work of Jensen and coworkers. In a study of the kinetics of the reversible reaction between chloral and various primary and secondary alcohols, Jensen, et al. (1970) found that the reaction in a nonpolar solvent was catalized by acetic acid. The product of reaction is the hemiacetal, as summarized by the following:



$$CCl_3\text{-}\overset{H}{C}=O + ROH \longrightarrow CCl_3\text{-}\underset{OR}{\overset{H}{C}}-OH$$

In the presence of water, chloral hydrate rather than chloral would likely be the reactant, but the hemiacetal could still be the final product. Whereas chloral hydrate would be expected to favor the aqueous phase strongly, it is likely that the hemiacetal of chloral and 2-ethyl hexanol would favor the alcohol phase. The observed high value of K_d could well be much more the result of the reaction to form the hemiacetal than of the transfer of chloral itself into the alcohol phase.

Additional Experiments.

Since the previous reports had shown carboxylic acids to be good catalysts for increasing the rate of reaction of chloral with various alcohols, we made several extractions of chloral using n-octanol to which several percent of various organic acids had been added. The procedure was the same as for the previous experiment, except the ethyl acetate and n-butyl acetate were not present in the initial aqueous phase and a sample taken after 60 minutes was the final sample analyzed.

The carboxylic acids chosen for testing were hexanoic, benzoic, and p-toluic. These acids are expected to show high values of K_d between water and octanol so that they should not be extracted back into the waste water to a large extent.

Additional Results and Discussion.

The results of the three additional experiments are reported in Table I2 in the form of apparent values of K_d. For comparison the previous results from the extraction of chloral hydrate with pure 2-ethyl hexanol are included in Table I2. The carboxylic acids are seen to have a significant catalytic effect, but not so great as to make this a very promising process approach. In a recycle process with solvent regeneration by distillation, other problems such as esterification of the carboxylic acid would have to be considered.

Table I2. Results from Extractions of Prepared Water Solutions Which Contained Chloral Hydrate

Initial water solutions contained 15,000 ppm of chloral hydrate.

Apparent values of K_d:

Time after beginning to shake funnel (min)	Run A	Run B	Run C	Run D
1	3.2	5.4	7.2	7.0
4	5.1	9.5	13.3	13.2
10	13.5	19.2	25.7	25.4
60	--	--	36.1	36.8
∞	38.5	--	--	--

Run A used pure 2-ethyl hexanol as solvent.

Run B used 1 wt. % hexanoic acid in n-octanol.

Run C used 2 wt. % benzoic acid in n-octanol.

Run D used 2 wt. % p-toluic acid in n-octanol.

APPENDIX J. METRIC CONVERSION TABLE

9.480×10^{-4} BTU = 1 joule
1.8 ^{o}F or ^{o}R = 1 ^{o}C or 1 ^{o}K
0.03281 ft = 1 cm
0.2642 gal = 1 liter
2.642×10^{-4} gal = 1 cm^3
1.341 HP = 1 kilowatt
0.3937 in = 1 cm
0.002205 lb = 1 gram
14.696 psi (lb/in^2) = 1 atm
14.223 psi (lb/in^2) = 1 kg./cm^2
14.504 psi (lb/in^2 = 1 bar